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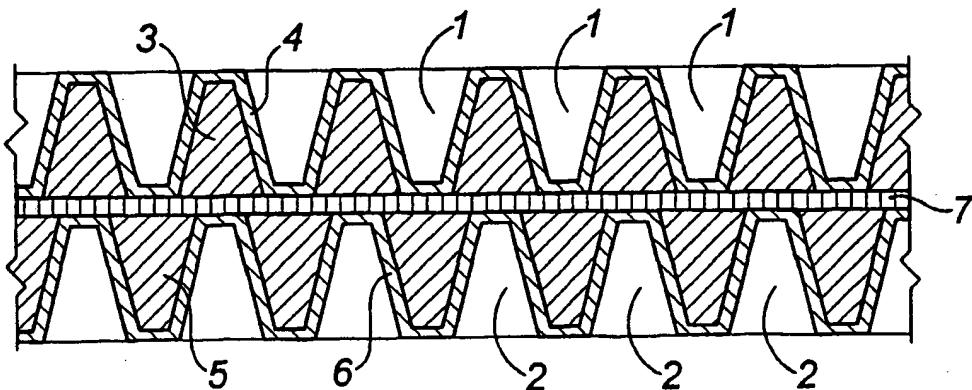
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(54) Title: METAL-SUPPORTED SOLID ELECTROLYTE ELECTROCHEMICAL CELL AND MULTI CELL REACTORS INCORPORATING SAME



(57) Abstract: The invention provides a metal-supported solid electrolyte electrochemical cell, multi cell reactor assemblies incorporating a plurality of such cells, and processes of forming the electrochemical cells. In one embodiment, the electrochemical cell includes a central electrolyte membrane, first and second perforated metallic layers adhered to each of the major surfaces of the central electrolyte membrane, and first and second outer, non-porous electrolyte layers formed above the metallic layers. In another embodiment, first and second inner, porous electrolyte layers are sandwiched on either side of the central membrane, between the first and second metallic layers. The electrochemical cell is thus generally formed from ceramic material as thin layers supported on non-porous, robust metallic layers, designed to behave as though made of metal. Preferably, the electrochemical cell includes metallurgically bonded electrical interconnects and/or gas seals.

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1           **METAL-SUPPORTED SOLID ELECTROLYTE ELECTROCHEMICAL CELL AND**  
2           **MULTI CELL REACTORS INCORPORATING SAME**

3           **FIELD OF THE INVENTION**

4           The present disclosure generally relates to electrochemical cells employing solid  
5           electrolytes where such solid electrolytes are ion conductors that conduct oxygen ions or protons  
6           or other ion species, or combinations of the foregoing. These solid electrolytes may exhibit  
7           exclusively ionic conductivity or a combination of ionic and electronic conductivity. Important  
8           applications of such electrochemical cells include solid oxide fuel cells, oxygen concentration  
9           cells, partial oxidation cells and reactor systems incorporating multiple cells.

10           **BACKGROUND OF THE INVENTION**

11           Of the known applications of solid electrolyte electrochemical cells the most important  
12           are based on oxygen ion conducting ceramic electrolytes, which are also called solid oxide  
13           electrolytes. These applications are solid oxide fuel cells, oxygen concentration cells, which are  
14           also known as oxygen pumps, and partial oxidation cells. Examples of solid oxide fuel cells are  
15           described in US Patent 4,490,445, US Patent 5,741,406 and US Patent 6,106,967. US Patent  
16           4,877,506 describes an oxygen pump. US Patent 5,681,373 describes a solid oxide cell suitable  
17           as an oxygen concentration or partial oxidation reactor. US Patent 5,770,326 describes a  
18           monolithic mass and energy transfer cell using solid oxide electrolytes suitable for all three of  
19           the aforementioned applications.

20           The discussion herein, of the merits of various solid electrolyte electrochemical cell  
21           designs, will focus on solid oxide fuel cells. However, one skilled in the art will readily  
22           recognize that the same or similar challenges arise in designing all types of solid electrolyte  
23           electrochemical cells. Fuel cells of all types, including Proton Exchange Membrane (PEM),  
24           Molten Carbonate (MCFC), Phosphoric Acid (PAFC), Alkaline (AFC) and Solid Oxide  
25           (SOFC), have recently been the focus of much development effort because they promise a more  
26           environmentally sustainable alternative to meeting the world's growing demand for electrical  
27           and mechanical energy than do energy conversion systems based on conventional combustion  
28           processes. Relative to competing fuel cell technologies, solid oxide fuel cells offer several  
29           advantages primarily related to their high operating temperature. The principal advantages of  
30           solid oxide fuel cells are high energy conversion efficiency, high quality byproduct heat, simpler  
31           fuel processing systems when using reformed hydrocarbon fuels, and avoidance of the  
32           expensive precious metal catalysts required in low temperature fuel cells.

The fundamental operation of all oxygen ion conducting solid oxide electrochemical cells is similar. Oxygen gas on the cathode side of a gas impermeable solid oxide electrolyte membrane is chemically reduced to oxygen ions, each carrying two extra electrons. These oxygen ions then migrate through the ionically conductive electrolyte membrane to the anode side of the cell where they may recombine to again form oxygen gas or may react with other gaseous species, such as by reacting with hydrogen to form water. For solid oxide electrolyte materials there is a strong direct relationship between ionic conductivity and temperature. Therefore, to achieve useful current densities the cell is typically operated at temperatures in the range of 600° C to 1100° C. In order that the oxidation reactions at the anode can proceed the surplus electrons carried by the oxygen ions must migrate back to the cathode side of the solid oxide membrane. The path by which the electrons on the anode side of the membrane migrate back to the cathode side may be either internal to the electrolyte membrane, external to the electrolyte membrane, or both. Where the electrolyte membrane exhibits both ionic and adequate electronic conductivity no external circuit is required to electrically connect the anode and cathode electrodes. Otherwise, such an external electrical circuit is required. In the case of a solid oxide fuel cell, the driving force for the electrochemical reactions is provided by the difference in the partial pressure of oxygen between the cathode and anode side of the cell which creates a voltage differential between the cathode and anode electrodes. Conversely, in the case of an oxygen pump an externally applied electrical bias is used to increase the partial pressure of oxygen on the anode side of the cell over that on the cathode side. If used as a partial oxidation cell, the driving force delivering oxygen to the anode side of the cell may be either an oxygen partial pressure difference, an external electrical bias or both.

23 All solid electrolyte electrochemical cells, including solid oxide fuel cells, are comprised  
24 of the same basic functional elements. The central element is a solid electrolyte membrane that  
25 is gas impermeable. Depending on the application, the electrolyte is designed to be exclusively  
26 an ionic conductor or a mixed ionic and electronic conductor. For solid oxide fuel cells, where  
27 the goal is to maximize the external voltage generated, the requirement is that the electrolyte  
28 membrane be, to the greatest extent possible, exclusively an ionic conductor. On either side of  
29 the electrolyte membrane and in intimate contact with it are electrode layers that have several  
30 functions. The electrodes must provide: a high density of reaction sites for the electrochemical  
31 reactions, ionically conductive pathways to conduct ion species between the reaction sites and  
32 the electrolyte membrane, electrically conductive pathways to conduct electrons to and from  
33 reaction sites to external current collectors, and unrestricted flow of gasses to and from reaction  
34 sites. To complete the cell the electrodes must be interconnected electrically and a gas

1 containment and transport means provided adjacent to each electrode to direct the different  
2 reacting gas streams to and from the appropriate electrode surfaces. To produce commercially  
3 useful systems multiple single cells are interconnected, typically in electrical series, and  
4 assembled into bundles for tubular cell designs or stacks for planar cell designs.

5 Minh, Ceramic Fuel Cells, Journal of the American Ceramics Society, 76[3] 563-88  
6 (1993) provides a useful review of the engineering challenges involved in designing solid oxide  
7 fuel cells and multi cell systems, and of the approaches that have been proposed to meet these  
8 challenges. Fundamentally, the difficulties in making commercially viable solid oxide fuel cells  
9 relate to the high temperatures required to achieve useful current density and to the fact that at  
10 least the electrolyte membrane is made of mechanically unforgiving ceramic materials. In most  
11 designs not only the electrolyte membrane but one or more of the cathode, the anode and the  
12 electrical interconnect element, used to electrically connect a number of individual cells  
13 together, are also made of mechanically unforgiving ceramic or cermet (ceramic-metal  
14 composite) materials. In addition to the limited ability of these ceramic materials to withstand  
15 direct tensile loads they also have very limited ability to withstand thermally induced stresses.  
16 This means that great care must be taken to minimize thermal gradients within the cell as well as  
17 thermal expansion mismatches between the different materials used to build the cell and the  
18 electrical interconnects and gas manifolds that must be connected to it. Finally, it is difficult to  
19 make reliable electrical connections to the porous ceramic cell electrodes and to provide reliable  
20 gas tight seals to keep fuel and oxidant gas streams from mixing.

21 In early solid oxide fuel cell designs the structural support for the cell was provided by a  
22 relatively thick dense ceramic electrolyte membrane, typically in the form of a flat plate or  
23 cylindrical tube, to which relatively thin anode and cathode electrodes were bonded. This  
24 provided a relatively simple structure but a long ionic conductor path length requiring operating  
25 temperatures of 1000° C or higher. More recently cell structures that permit the thickness of the  
26 electrolyte membrane to be reduced to the range of 10  $\mu\text{m}$  or less have been demonstrated to  
27 provide useful current densities at operating temperatures in the range of 600° C to 800° C. To  
28 accommodate a thin electrolyte membrane requires that either the anode or cathode must now  
29 provide the structural support for the cell and so must be made relatively thick. However, the  
30 thick supporting electrode must also provide unrestricted access for the reacting gases to reach  
31 close to the electrolyte membrane in order to maintain the desired short ionic conductor path  
32 length. The consequence is that the supporting electrode must be made both thick and highly  
33 porous. This in turn complicates the realization of a gas impermeable electrolyte membrane

1 since it is difficult to build a thin gas impermeable ceramic layer by deposition on or lamination  
2 to a porous substrate.

3       While anode or cathode supported solid oxide fuel cells with thin electrolyte membranes  
4 and operating at temperatures below 800° C have less stringent materials selection requirements  
5 than their thick electrolyte membrane predecessors, these cell designs continue to exhibit a  
6 number of deficiencies that significantly limit their commercial potential. The fact that at least  
7 the electrode providing structural support to the cell must be relatively thick means that gas  
8 transport, to and from the interface between the electrolyte membrane and the electrode, through  
9 this porous electrode is restricted. In the extreme, this mass transport limitation can become the  
10 rate-limiting factor for the cell's electrochemical reactions resulting in increased electrode  
11 overpotential losses. Increased electrode overpotential causes reduced voltage output and  
12 reduced efficiency for the cell.

13       No means has yet been found to provide solid oxide fuel cells with reliable gas seals.  
14 The prior art teaches two basic approaches: a mechanical compression seal using a pliant high  
15 temperature sealing gasket, and glass seals such as are used to make the glass to metal seal in  
16 light bulbs. Neither approach produces a seal that can withstand rapid thermal cycling or  
17 significant pressure differentials.

18       Neither does the prior art teach how to make durable low resistance electrical  
19 connections to the cell electrodes. The conventional approach is a surface to surface  
20 compression contact where the contact interface is subject to significant change and degradation  
21 in electrical performance, occurring over time at the cell's operating temperature. Since each  
22 individual cell requires two such connections the resistive voltage losses for a stack of cells  
23 connected in electrical series increase as the number of cells in the stack increases. Therefore,  
24 the voltage output of a fuel cell stack is significantly less than the sum of the voltage output  
25 from its individual constituent cells.

26       US Patent 3,464,861 and US Patent 5,328,779 teach solid oxide fuel cells supported on  
27 porous metal and/or intermetallic electrodes wherein these electrodes may be sufficiently robust  
28 electrical conductors to enable electrical interconnect at the electrode's outer perimeter rather  
29 than by surface to surface contact across its active surface. However, these cells are  
30 manufactured by thermal spray processes that are limited to producing relatively thick central  
31 electrolyte membranes that require cell operating temperatures above 800° C to achieve useful  
32 current densities. These high operating temperatures make the use of porous metal support  
33 electrodes infeasible because of continued sintering of the porous metal resulting in loss of  
34 electrode activity, volatilization of chromium oxide from electrically conductive oxide scale on

1 the surface of the metal which then poisons electrochemically active sites, growth of electrically  
2 resistive oxide scale on the surface of the metal resulting in high internal cell resistance, or a  
3 combination of two or more of these effects.

4 Even with reduced operating temperatures, prior art solid oxide fuel cells must be started  
5 up slowly, especially if starting from ambient temperature. This results because the cell's  
6 structural characteristics are dominated by the thermal shock behaviour of the ceramic materials  
7 incorporated therein. This slow startup performance is a major impediment to the adoption of  
8 solid oxide fuel cells for transportation applications. Another important consequence of having  
9 to limit thermal gradients within a solid oxide fuel cell is the requirement to limit the difference  
10 in temperature between incoming and outgoing air to about 100° C. Air is typically used both as  
11 the source of oxygen for the cathode electrode and as the means to remove the surplus heat  
12 produced by the electrochemical reactions. By limiting the allowable temperature gain for the  
13 air passing through the cell to about 100° C, 3 to 5 times more air than is required to deliver the  
14 required amount of oxygen must be used. Consequently, the air handling system is larger than  
15 would otherwise be required resulting in increased system capital costs and reduced system  
16 efficiency.

17 Thermal management is in fact a very significant issue in practical solid electrolyte  
18 electrochemical cell reactors since the electrochemical reactions typically generate a lot of  
19 surplus heat. As already stated, the conventional approach to thermal management in solid  
20 oxide fuel cells is to blow surplus air through the stack, which air can contact and remove heat  
21 from the cathode surfaces. By a series of heat exchangers, the heated exhaust air is then used to  
22 preheat incoming fuel gas and/or incoming air. Even if the fuel cell stack could tolerate a larger  
23 differential in temperature between the incoming and outgoing air, a large volume of cooling air  
24 must be circulated since air is not a good heat transfer fluid. Also, as the volume specific  
25 current density of a solid oxide fuel cell stack increases, as is desirable to minimize size and  
26 cost, the volume specific mass of circulating heat transfer fluid must also increase. Therefore it  
27 is desirable that solid oxide fuel cell stacks be compatible with the use of liquid heat transfer  
28 fluids as this could make possible significant reductions in the size of the thermal management  
29 system. However, using liquid heat transfer fluids in conventional solid oxide fuel cell stacks  
30 would generate intolerable thermal gradients resulting in mechanical failure of the individual  
31 cells and/or the gas seals.

32 Considering thermal management in the context of minimizing thermally induced  
33 stresses in individual cells, which is desirable for long cell life even where the cell can tolerate  
34 significant thermal gradients, prior art solid electrolyte electrochemical cells do not provide a

1 means to compensate for differences in the <sup>6</sup> concentration and/or temperature of the reacting  
2 gases at different areas over the cell surface. Such differences in the concentration and/or  
3 temperature of the reacting gases as they are delivered to the cell may cause areas of increased  
4 or decreased electrochemical activity relative to the average electrochemical activity over the  
5 complete area of the cell. These differences in electrochemical activity can, in turn, magnify  
6 preexisting temperature differences or translate gas concentration differences into temperature  
7 differences, thus contributing to or causing thermal gradients.

8 In prior art solid oxide fuel cells using cermet anode materials, such as the commonly  
9 used nickel and yttria stabilized zirconia composite, cell performance is seriously reduced by  
10 even trace amounts of sulphur impurities in the fuel gas. The exposed metal surfaces are  
11 quickly attacked by sulphur destroying their catalytic activity. Neither are conventional cermet  
12 anodes tolerant to fuel gas interruptions and consequent exposure to oxidizing atmospheres at  
13 the cell operating temperature. In this case the nickel metal is quickly oxidized resulting in a  
14 severe loss in electrical conductivity for the anode electrode. Likewise, conventional cermet  
15 anodes cannot be switched sequentially from anode to cathode operation as would be useful to  
16 burn off accumulated carbon deposits that may result when the cell is run on hydrocarbon fuel.

17 Although it is possible and desirable to reform hydrocarbon fuel directly on the anode  
18 electrode of a solid oxide fuel cell, and this is desirable since it provides the closest possible  
19 thermal integration between the exothermic electrochemical reactions and the endothermic  
20 reforming reactions, it is difficult to achieve in practice. This is particularly true with heavier  
21 hydrocarbon fuels such as gasoline because of the carbon build-up issue described already and  
22 also because of inadequate catalytic activity to facilitate the reforming reactions. It would  
23 therefore be advantageous to incorporate specialized reforming catalysts, which may be fuel  
24 specific, into or onto the surface of the anode electrode. However, this is difficult to accomplish  
25 on porous anode electrodes where open interconnected porosity must also be maintained.

## 26 SUMMARY OF THE INVENTION

27 Accordingly, the inventors have recognized a need for improved solid electrolyte  
28 electrochemical cells and multi cell reactors providing:

29

- 30 • Thin, preferably less than 10  $\mu\text{m}$  thick, yet robust electrolyte membranes that enable  
31 reduced cell ionic resistance and useful current density at operating temperatures at  
or below 800° C and preferably at temperatures below 650° C;
- 32 • An open, non-porous electrode structure that minimizes the mass transport  
33 limitations associated with porous electrodes, thus reducing cell overpotential losses,

1 and facilitating the incorporation<sup>7</sup> of specialized catalysts into or onto the electrode  
2 surface;

- 3     • Reliable gas seals and electrical interconnects;
- 4     • The ability to withstand significant thermal gradients, thus permitting fast start-up
- 5         and shut-down;
- 6     • Electrodes that can operate interchangeably as a cathode or anode, thus providing
- 7         tolerance for operating upsets and permitting the burn-off of contaminants such as
- 8         carbon, which can accumulate on and disrupt the operation of anode electrodes when
- 9         such anode electrodes are operated in the presence of hydrocarbon gas;
- 10    • The ability to deliberately provide differences in electrochemical activity between
- 11         different areas across the cell's surface so as to compensate for differences in the
- 12         concentration and/or temperature of reacting gasses at such different areas and
- 13         thereby limit thermal gradients over the whole area of the cell; and
- 14    • The ability to use liquid heat transfer fluids to facilitate thermal management of multi
- 15         cell reactors.

16 Broadly, the present invention provides a flexible, metal-supported, solid electrolyte  
17 electrochemical cell comprising:

18 a) a central, non-porous, ionically- or mixed ionically- and electronically-conducting  
19 electrolyte membrane which is less than 10  $\mu\text{m}$  thick and defines two major surfaces,  
20 one major surface on each side of the central electrolyte membrane;

21 b) a first, non-porous, metallic layer which is adhered to one of the major surfaces of the  
22 central electrolyte membrane, and having a plurality of perforations extending  
23 therethrough forming a first pattern of perforations;

24 c) a second, non-porous, metallic layer which is adhered to the other of the major surfaces  
25 of the central electrolyte membrane, and having a plurality of perforations extending  
26 therethrough forming a second pattern of perforations;

27 d) a first outer, non-porous, ionically- or mixed ionically- and electronically-conducting  
28 electrolyte layer which is:  
29 - adhered to the first metallic layer and makes intimate contact with the central  
30 electrolyte membrane through the first pattern of perforations, and

8

- continuously ionically-conductive throughout its bulk, and electronically-conductive through its thickness from the underlying first metallic layer to any reacting gases at its outer surface;
- e) a first, ionically-conductive, interface formed at a contact surface between the first outer electrolyte layer and the central electrolyte membrane;
- f) a first, electronically-conductive, interface formed at a contact surface between the first metallic layer and the first outer electrolyte layer;
- g) a second outer, non-porous, ionically- or mixed ionically- and electronically-conducting electrolyte layer which is:
  - adhered to the outer surface of the second metallic layer and makes intimate contact with the central electrolyte membrane through the second pattern of perforations, and
  - continuously ionically-conductive throughout its bulk, and electronically-conductive through its thickness from the underlying second metallic layer to any reacting gases at its outer surface;
- h) a second, ionically-conductive interface formed at a contact surface between the second outer electrolyte layer and the central electrolyte membrane; and
- i) a second, electronically-conductive interface formed at a contact surface between the second metallic layer and the second outer electrolyte layer.

The invention also extends to flexible metal-supported solid electrolyte electrochemical cell substantially as above, but having, instead of the first and second porous, outer electrolyte layers, first and second porous, inner electrolyte layers formed between the metallic layers and the central electrolyte membrane.

The invention also broadly provides reactor assemblies with a plurality of the flexible metal-supported solid electrolyte electrochemical cells connected together in electrical series, and to processes to produce the flexible metal-supported solid electrolyte electrochemical cells.

#### 26 BRIEF DESCRIPTION OF THE DRAWINGS

27 Fig. 1a shows a plan view of a segment of a typical metal-supported solid electrolyte  
28 electrochemical cell of the present invention;

29 Fig. 1b shows a cross sectional view along line A-A of Fig. 1a;

1        Fig. 2a shows an expanded cross sectional view of a typical metal-supported solid  
2        electrolyte electrochemical cell illustrating details of the ionically- and electronically-conductive  
3        interfaces and representative reactions for such a cell operated as a solid oxide fuel cell;

4        Fig. 3a shows a plan view of a multi cell reactor incorporating multiple metal-supported  
5        solid electrolyte electrochemical cells and metallic interconnect elements;

6        Fig. 3b shows a cross sectional view along line A-A of Fig. 3a;

7        Fig. 4a is a cross sectional view along line b-b of Fig. 3a, showing a multi cell reactor  
8        incorporating multiple metal-supported solid electrolyte electrochemical cells that illustrates  
9        schematically how the gas flow channels adjacent to the cell surfaces are connected to gas  
10      supply and exhaust manifolds;

11      Fig. 4b is an expanded cross sectional view of the detail in circle C of Fig. 3b showing a  
12      metallurgically bonded interconnection and gas seal;

13      Fig. 5a shows a plan view of representative patterns of perforations in the metallic layers  
14      in which the patterns of perforations overlap so that areas of the central electrolyte membrane  
15      are exposed and not supported by either metallic layer;

16      Fig. 5b is an expanded cross sectional view of the detail in circle A in Fig. 5a;

17      Fig. 6a shows a schematic layout of a metal-supported solid electrolyte electrochemical  
18      cell reactor assembly, wherein the legend for the gas supply and exhaust manifolds is taken  
19      along line X-X of Fig. 6a;

20      Fig. 6b is a cross sectional view taken along line A-A of Figure 6a;

21      Fig. 6c is a cross sectional view taken along line B-B of Fig. 6a;

22      Fig. 7a shows a schematic layout of a dimpled metallic interconnect element, with  $\cap$   
23      denoting top side (raised) dimples and  $\cup$  representing bottom side (depressed) dimples;

24      Fig. 7b is a cross sectional view along line A-A of Fig. 7a;

25      Fig. 8 shows a flow chart summarizing a representative manufacturing process for  
26      building a reactor assembly incorporating metal-supported solid electrolyte electrochemical  
27      cells;

28      Fig. 9 is an expanded cross sectional view of a second embodiment of the invention,  
29      showing a typical metal-supported solid electrolyte electrochemical cell with porous inner  
30      electrolyte layers operating as a solid oxide fuel cell and illustrating the gas flow pathways for  
31      such a cell; and

1 Fig. 10 shows a flow chart summarizing a representative manufacturing process for  
2 building a reactor assembly incorporating metal-supported solid electrolyte electrochemical cells  
3 having the porous inner electrolyte layers of the second embodiment.

#### 4 DESCRIPTION OF THE PREFERRED EMBODIMENT

##### 5 Metal-Supported Solid Electrolyte Electrochemical Cell And Multi Cell Reactor Assembly 6 Incorporating Same

###### 7 a) Overview

8 The invention extends to metal-supported solid electrolyte electrochemical cell and multi  
9 cell reactors (or reactor assemblies) incorporating such cells. In a preferred embodiment a  
10 metal-supported solid electrolyte electrochemical cell incorporating metallurgically bonded  
11 electrical interconnects and/or gas seals is provided. From a structural perspective, this metal-  
12 supported solid electrolyte cell, by incorporating all the ceramic materials as thin layers  
13 supported on non-porous, robust metallic layers, is designed to behave as though it were made  
14 of metal. Thus, the mechanical difficulties arising with brittle ceramic structures can be  
15 eliminated or significantly reduced. In particular, the solid electrolyte electrochemical cells  
16 described herein are capable of tolerating significant thermal gradients. In addition, since the  
17 electronic conductors in both electrodes are predominantly metallic, electronic resistive losses  
18 within the cell are minimized and the electronic resistive loss penalty associated with reduced  
19 operating temperature is significantly reduced. These losses are significant for electrodes made  
20 only of electronically conductive ceramics. In this context it should be understood that the  
21 metallic layers may be comprised of individual metals and/or alloys and/or layered composites  
22 comprising one or more different metals and/or one or more different alloys. The metallic  
23 layers may also comprise, dispersed throughout their bulk and/or at their surfaces, a minor  
24 amount of one or more discontinuous ceramic phases provided that the predominantly metallic  
25 nature, in terms of mechanical and electrical conductivity properties, of the metallic layers is  
26 preserved.

27 As used herein to describe the metallic and/or ceramic layers of the metal-supported  
28 solid electrolyte electrochemical cell, the terms "non porous", "non-porous" and "dense" do not  
29 mean that these layers have no porosity but rather that these layers do not exhibit interconnected  
30 through porosity, and consequently are gas impermeable. A fundamental prerequisite for such a  
31 metal-supported solid electrolyte cell is that the metals or alloys used provide sufficient  
32 mechanical strength and stability, e.g. oxidation resistance, at the cell operating temperature or  
33 that the operating temperature of the cell be reduced such that this requirement is satisfied. The

1      cell operating temperature can be reduced by - using electrolyte materials exhibiting higher ionic  
2      conductivity, and/or shortening the average length of the ionic conductor path between the  
3      electrochemically active sites on the anode side of the cell and the electrochemically active sites  
4      on the cathode side of the cell.

5      b)      **Description of First Embodiment**

6      In a first embodiment, the metal-supported solid electrolyte electrochemical cell  
7      includes a central electrolyte membrane defining two major surfaces, one major surface on each  
8      side of the electrolyte membrane. Adhered to one major surface of the central electrolyte  
9      membrane is a first metallic layer which is formed with a first pattern of perforations. Adhered  
10     to the other major surface of the central electrolyte membrane is a second metallic layer, the  
11     second metallic layer forming a second pattern of perforations. Adhered to the outer surface,  
12     that is the surface not adhered to the central electrolyte membrane, of the first metallic layer is a  
13     first outer electrolyte layer that makes intimate contact with the central electrolyte membrane  
14     where such membrane is exposed by the first pattern of perforations. The interface between the  
15     first outer electrolyte layer and the central electrolyte membrane defines a first ionically  
16     conductive interface. The interface between the first metallic layer and the first outer electrolyte  
17     layer defines a first electrically conductive interface. Adhered to the outer surface, that is the  
18     surface not adhered to the central electrolyte membrane, of the second metallic layer is a second  
19     outer electrolyte layer that makes intimate contact with the central electrolyte membrane where  
20     such membrane is exposed by the second pattern of perforations. The interface between the  
21     second outer electrolyte layer and the central electrolyte membrane defines a second ionically  
22     conductive interface. The interface between the second metallic layer and the second outer  
23     electrolyte layer defines a second electrically conductive interface.

24     The cell is completed by providing metallic interconnect elements, including gas seals  
25     and electrical interconnects, to conduct reacting gases to and from each side of the metal-  
26     supported solid electrolyte membrane and to electrically connect the first metallic layer to the  
27     second metallic layer through an external electrical circuit.

28     The central electrolyte membrane, the first outer electrolyte layer and the second outer  
29     electrolyte layer may be exclusively ionic conductors or may be mixed ionic and electronic  
30     conductors. The central electrolyte membrane, the first outer electrolyte layer and the second  
31     outer electrolyte layer may each be comprised of a single electrolyte material, a mixture of  
32     different electrolyte materials, a layered composite of different electrolyte materials, or a  
33     combination of all of the foregoing. Each of the first outer electrolyte layer and the second outer  
34     electrolyte layer includes a continuous ionically conductive phase throughout and in addition

1 provides an electronically conductive path, through its thickness, from the adjacent underlying  
2 electrically conductive interface to the reacting gases at its outer surface. Where the first outer  
3 electrolyte layer and/or the second outer electrolyte layers is formed predominantly of ionically  
4 conductive phases, the layer is made sufficiently thin to permit electrons to migrate through its  
5 thickness. Preferably, the first and second outer electrolyte layers include one or more  
6 electrolyte phases that exhibit both ionic and electronic conductivity, or comprise a multi phase  
7 mixture of one or more predominantly ionically conducting and one or more predominantly  
8 electronically conducting phases, or comprise a combination of the foregoing.

9 This first embodiment is illustrated generally in Fig. 1 – Fig. 8, and is described below in  
10 greater detail.

11 Fig. 1a and 1b show a schematic plan view of a segment of a typical metal-supported  
12 solid electrolyte electrochemical cell as well as a schematic cross sectional view through such a  
13 cell. The first pattern of perforations 1 are shown penetrating through the first metallic layer 3  
14 and the second pattern of perforations 2 are shown penetrating through the second metallic layer  
15 5. As illustrated in Fig. 1a, 1b, the perforations may be conical in shape and the first pattern of  
16 perforations 1 may be offset from the second pattern of perforations 2 (i.e., they are not aligned)  
17 such that the central electrolyte membrane 7 is everywhere supported by either the first metallic  
18 layer 3 or the second metallic layer 5. In Fig. 5a, 5b, the first and second perforations 1, 2 are  
19 shown in an overlapping, partially aligned arrangement, so that areas of the central electrolyte  
20 membrane 7 are exposed in the aligned areas. However, the perforations may be of any shape  
21 and arranged in many different patterns as long as adequate structural support is everywhere  
22 provided to the central electrolyte membrane. The first outer electrolyte layer 4 is shown to  
23 completely cover that surface of the first metallic layer 3 which is not in contact with the central  
24 electrolyte membrane 7 and to cover the central electrolyte membrane 7 where it is exposed by  
25 the first pattern of perforations 1. Likewise, the second outer electrolyte layer 6 is shown to  
26 completely cover that surface of the second metallic layer 5 not in contact with the central  
27 electrolyte membrane 7 and to cover the central electrolyte membrane 7 where it is exposed by  
28 the second pattern of perforations 2. While it may be desirable, it is not essential that the outer  
29 electrolyte layers cover the central electrolyte membrane where the membrane is exposed by the  
30 first and second pattern of perforations.

31 Fig. 3a and 3b show a schematic plan view and a schematic sectional view of a multi cell  
32 reactor incorporating metal-supported solid electrolyte electrochemical cells and metallic  
33 interconnect elements. The interconnect elements 12, 13 and 14, provide both series electrical  
34 interconnection between the stacked cells and gas flow channels to transport the relevant gases

1 to and from the electrode surfaces. Fig. 4a and 4b show different sectional views of this same  
2 reactor. It should be noted that, to ensure clarity, the first and second pattern of perforations and  
3 the first and second outer electrolyte layers are not shown in these drawings although it is to be  
4 understood that they are present. The peripheral gas seals, the electrical interconnects 13, and/or  
5 the interior interconnects 14 may be made by several techniques, alone or in combination with  
6 each other. Firstly they may be made by direct compression contact between the first metallic  
7 layer 3 and/or the second metallic layer 5 and the metallic interconnect element 12.  
8 Alternatively they may be made by compression contact to a pliant metallic gasket inserted  
9 between the first metallic layer 3 and/or the second metallic layer 5 and the metallic interconnect  
10 element 12. Alternatively they may be made by metallurgically bonding the first metallic layer  
11 3 and/or the second metallic layer 5 to the metallic interconnect element 12. The preferred  
12 approach, which is described in more detail below, is to make at least the peripheral gas seal and  
13 electrical interconnects 13 by metallurgically bonding both the first metallic layer 3 and the  
14 second metallic layer 5 to the metallic interconnect elements 12.

15 Fig. 3a, 3b, 4a and 4b also illustrate an important detail for maintaining electrical  
16 isolation between the first metallic layer 3 and the second metallic layer 5 at the perimeter  
17 and/or at the edge of openings through the metal-supported cell. Where such electrical isolation  
18 is desired, the central electrolyte membrane 7 is selected to provide little or no electronic  
19 conductivity, and can therefore be considered as an electrical insulator. Electrical isolation at  
20 the perimeter of the cell and/or at the edge of openings through the cell is provided by  
21 deliberately extending the central electrolyte membrane 7 beyond the termination of at least one  
22 of the first metallic layer 3 or the second metallic layer 5. As shown in Fig. 3a, 3b, 4a and 4b,  
23 the central electrolyte membrane 7 extends beyond the termination of the first metallic layer 3.

24 As represented in Fig. 3a, 3b, 4a and 4b, the metal-supported solid electrolyte  
25 electrochemical cells and their associated metallic interconnect elements are shown to be both  
26 planar and rectangular in shape. By "planar" is meant that each cell occupies a single plane and  
27 all the cells and the metallic interconnect elements in the reactor are arranged in a series of  
28 parallel planes. However, since both the individual cells and the metallic interconnect elements  
29 are thin and flexible, they in fact exist as complex curved surfaces. The plan projection of the  
30 outer perimeter of an individual metal-supported cell and its associated metallic interconnect  
31 elements may be of any shape including, for example, circular, square, rectangular and  
32 hexagonal. Within this outer perimeter the cell may or may not have openings or holes to  
33 accommodate gas supply and exhaust manifolds that intersect the surface of the cell. The  
34 primary considerations in selecting the shape for metal-supported cells are minimization of

1 electronic conductor path length from anode to cathode, ease of integration with gas supply and  
2 exhaust manifolds, ease and maximization of material utilization in manufacturing, and ready  
3 scale-up of the cell to larger size. A rectangular shaped cell with gas supply and exhaust  
4 manifolds arranged at the perimeter along both long sides provides for all of the foregoing  
5 objectives and is, therefore, a preferred shape and gas manifolding arrangement for metal-  
6 supported solid electrolyte electrochemical cells.

7 In Fig. 3a and 3b, the ribbed structure shown for the metallic interconnect element 12  
8 provides both the means to achieve interior interconnects 14, which may reduce cell electrical  
9 resistance or provide additional mechanical support to the cell or both, and the means to  
10 maintain open gas flow channels 15 that are connected to and communicate with the gas supply  
11 and exhaust manifolds 16. The metallic interconnect element 12 may incorporate any pattern of  
12 raised or depressed ridges and/or dimples so long as these accomplish the purpose of  
13 maintaining unrestricted gas flow channels to and from the electrode surfaces and communicate  
14 effectively with the gas supply and exhaust manifolds. Preferred patterns of ridges and dimples  
15 are those that readily permit the metallic interconnect element 12 to be formed most  
16 economically, such as by stamping from a thin metal sheet, and provide ease of interconnection  
17 and communication with the gas supply and exhaust manifolds. For these reasons, a dimpled  
18 pattern of bumps is preferred, wherein each side of the metallic interconnect element has a  
19 pattern of raised bumps, and the dimple pattern on one side of the metallic interconnect element  
20 12 is offset from, and interspersed with, the dimple pattern on the other side of the metallic  
21 interconnect element 12. Such a dimpled metallic interconnect element 12 is illustrated in  
22 Fig. 7a, 7b, where dimensions S1 and S2 are largely dependent on dimension T and typically  
23 range from about 1 mm to about 20 mm. More preferably dimensions S1 and S2 range from  
24 about 2 mm to about 10 mm.

25 It should also be noted that the gas supply and exhaust manifolds 16, as shown in  
26 Fig. 3a, 3b, 4a, and 4b, are arranged for schematic simplicity only, such that the functioning of  
27 the metallic interconnect elements 12 might be more clearly illustrated. The preferred  
28 arrangement for the gas supply and exhaust manifolds 16 is to integrate them as axial channels  
29 located around but inside the perimeter of the reactor. This manifolding arrangement is  
30 conventionally known as internal manifolding and is illustrated in the design of the dimpled  
31 metallic interconnect element shown in Fig. 7a, 7b.

32 The operation of the metal-supported solid electrolyte electrochemical cell of the present  
33 invention is fundamentally the same as for conventional solid electrolyte electrochemical cells.  
34 However, the details of the ionic conductor pathway and in particular of the electronic conductor

1 pathway from the cathode to the anode differ. To illustrate, consider the example where a cell  
2 of the present invention is operated as a solid oxide fuel cell wherein the central electrolyte layer  
3 is exclusively an ionic conductor and the outer electrolyte layers are mixed ionic and electronic  
4 conductors. Further, let it be assumed that the first outer electrolyte layer is in contact with an  
5 oxygen rich gas and the second outer electrolyte layer is in contact with a fuel gas such as  
6 hydrogen. Consequently, the first outer electrolyte layer in combination with the first  
7 electrically conductive interface and the first metallic layer operates as the cathode electrode,  
8 and the second outer electrolyte layer in combination with the second electrically conductive  
9 interface and the second metallic layer operates as the anode electrode. As the first outer  
10 electrolyte layer is a mixed conductor, electrons, oxygen ions and adsorbed oxygen gas can  
11 come into intimate contact at all points on its surface. Likewise, as the second outer electrolyte  
12 layer is a mixed conductor, electrons, oxygen ions and adsorbed hydrogen fuel gas can come  
13 into intimate contact at all points on its surface. On the cathode side, electrons migrate from the  
14 underlying first metallic layer through the first electronically conductive interface and through  
15 the thickness of the first outer electrolyte layer to the surface of the first outer electrolyte layer  
16 where they combine with and ionize adsorbed oxygen. The oxygen ions then migrate along the  
17 first outer electrolyte layer until they pass through the first ionically conductive interface and  
18 into the central electrolyte membrane where the central electrolyte membrane contacts the first  
19 outer electrolyte layer at the first pattern of perforations in the first metallic layer. The oxygen  
20 ions then migrate through the central electrolyte layer and enter the second outer electrolyte  
21 layer through the second ionically conductive interface where the second outer electrolyte layer  
22 contacts the central electrolyte membrane at the second pattern of perforations in the second  
23 metallic layer. The oxygen ions then migrate to the surface of the second outer electrolyte layer  
24 where they come into contact with and react with the adsorbed hydrogen fuel gas liberating two  
25 electrons. These electrons then migrate through the thickness of the second outer electrolyte layer  
26 and through the second electronically conductive interface and into the second metallic  
27 layer. Once in the second metallic layer these electrons then migrate back to the first metallic  
28 layer through an external electrical circuit (not shown).

29 Fig. 2 shows an schematic expanded cross sectional view of a metal-supported solid  
30 electrolyte electrochemical cell and illustrative reactions and conductor paths for such a cell  
31 operating as a solid oxide fuel cell. As illustrated, the first metallic layer 3, in combination with  
32 the first outer electrolyte layer 4 and the first electrically conductive interface 9, operate as the  
33 cathode electrode. The second metallic layer 5, in combination with the second outer electrolyte  
34 layer 6 and the second electrically conductive interface 11, operate as the anode electrode.

1 Oxygen ions form on the surface of, and migrate through, the first outer electrolyte layer 4, pass  
2 into the central electrolyte membrane 7 through the first ionically conductive interface 8, travel  
3 through the central electrolyte membrane 7, pass through the second ionically conductive  
4 interface 10 into the second outer electrolyte layer 6, and migrate to the surface of the second  
5 electrolyte layer where they react with fuel gas to liberate their surplus electrons. The electrons  
6 liberated on the surface of the second outer electrolyte layer 6 migrate into the second metallic  
7 layer 5 through the second electrically conductive interface 11, travel by an external electrical  
8 circuit (not shown) connecting the second metallic layer 5 to the first metallic layer 3, pass into  
9 the first outer electrolyte layer 4 through the first electrically conductive interface 9, and migrate  
10 to the surface of the first outer electrolyte layer 4 where they combine with adsorbed oxygen to  
11 form oxygen ions. The outer electrolyte layers are preferably mixed ionic and electronic  
12 conductors. However, if the outer electrolyte layer is thin enough such that electrons can tunnel  
13 through to the electrically conductive interface then the outer electrolyte layers may exhibit only  
14 ionic conductivity. To achieve stable and robust ionically conductive pathways through the cell,  
15 the first and second ionically conductive interfaces should provide continuous, intimate and  
16 adherent contact between the outer electrolyte layers and the central electrolyte membrane, and  
17 the first and second outer electrolyte layers should be dense and crack free. These are key  
18 challenges in building the metal-supported cell. Similarly, the integrity of the first and second  
19 electrically conductive interfaces is critical to achieving reduced electrical resistance for the cell  
20 and is a very important consideration in selecting materials for the first and second metallic  
21 layers.

22 **c) Description of Second Embodiment**

23 In a second embodiment of the invention, the metal-supported solid electrolyte  
24 electrochemical cell includes a central electrolyte membrane defining two major surfaces, one  
25 major surface on each side of the electrolyte membrane. Adhered to one major surface of the  
26 central electrolyte membrane is a first porous inner electrolyte layer. To that surface of the first  
27 porous inner electrolyte layer which is not adhered to the central electrolyte membrane, is  
28 adhered a first metallic layer which incorporates a first pattern of perforations. The interface  
29 between the central electrolyte membrane and the first porous inner electrolyte layer defines a  
30 first inner ionically conductive interface. The interface between the first porous inner  
31 electrolyte layer and the first metallic layer defines a first inner electrically conductive interface.  
32 Adhered to the other major surface of the central electrolyte membrane is a second porous inner  
33 electrolyte layer. To that surface of the second porous inner electrolyte layer not adhered to the  
34 central electrolyte membrane is adhered a second metallic layer, said second metallic layer

17

1 incorporating a second pattern of perforations. The interface between the central electrolyte  
2 membrane and the second porous inner electrolyte layer defines a second inner ionically  
3 conductive interface. The interface between the second porous inner electrolyte layer and the  
4 second metallic layer defines a second inner electrically conductive interface. Adhered to the  
5 outer surface, that is the surface which is not adhered to the first porous inner electrolyte layer,  
6 of the first metallic layer may or may not be a first outer electrolyte layer which makes intimate  
7 contact with the first porous inner electrolyte layer where such porous electrolyte layer is  
8 exposed by the first pattern of perforations. The interface between the first outer electrolyte  
9 layer and the first porous inner electrolyte layer defines a first porous ionically conductive  
10 interface. The interface between the first metallic layer and the first outer electrolyte layer  
11 defines a first electrically conductive interface. Adhered to the outer surface, that is the surface  
12 which is not adhered to the second porous inner electrolyte layer, of the second metallic layer  
13 may or may not be a second outer electrolyte layer which makes intimate contact with the  
14 second porous inner electrolyte layer where such porous electrolyte layer is exposed by the  
15 second pattern of perforations. The interface between the second outer electrolyte layer and the  
16 second porous inner electrolyte layer defines a second porous ionically conductive interface.  
17 The interface between the second metallic layer and the second outer electrolyte layer defines a  
18 second electrically conductive interface.

19 The cell is completed by providing metallic interconnect elements, including gas seals  
20 and electrical interconnects, to conduct reacting gases to and from each side of the metal-  
21 supported solid electrolyte membrane and to electrically connect the first metallic layer to the  
22 second metallic layer through an external electrical circuit. The central electrolyte membrane,  
23 the first porous inner electrolyte layer, the second porous inner electrolyte layer, the first outer  
24 electrolyte layer and the second outer electrolyte layer may be comprised of exclusively ionic  
25 conductors or of mixed ionic and electronic conductors. The central electrolyte membrane, the  
26 first porous inner electrolyte layer, the second porous inner electrolyte layer, the first outer  
27 electrolyte layer and the second outer electrolyte layer may each be formed of a single  
28 electrolyte material, a mixture of different electrolyte materials, a layered composite of different  
29 electrolyte materials, or a combination of the foregoing. Preferably, the first and second porous  
30 inner electrolyte layers and the first and second outer electrolyte layers are each formed of one  
31 or more electrolyte phases that exhibit both ionic and electronic conductivity, or are each formed  
32 of a multi phase mixture of one or more predominantly ionically conducting and one or more  
33 predominantly electronically conducting phases, or each are formed of a combination of the  
34 foregoing. The first and second porous inner electrolyte layers and the first and second porous

- 1 ionically conductive interfaces are designed to be gas permeable to permit ready transport of
- 2 reacting gases into, through and out of the porous inner electrolyte layers.

3       In accordance with this second embodiment of the invention, the fundamental operation  
4 of a metal-supported solid electrolyte electrochemical cell incorporating porous inner electrolyte  
5 layers is similar to that of conventional solid electrolyte electrochemical cells. However, the  
6 details of the electrode structures differ.

7       To illustrate, consider the example where a cell of the present invention is operated as a  
8 solid oxide fuel cell wherein the central electrolyte membrane is exclusively an ionic conductor  
9 and the porous inner electrolyte layers are mixed ionic and electronic conductors. For  
10 simplicity, assume that the cell does not incorporate outer electrolyte layers. Further, let it be  
11 assumed that the first metallic layer and the first porous inner electrolyte layer are in contact  
12 with an oxygen rich gas and the second metallic layer and the first porous inner electrolyte layer  
13 are in contact with a fuel gas such as hydrogen. Consequently, the first porous inner electrolyte  
14 layer in combination with the first metallic layer and its first pattern of perforations, the first  
15 inner ionically conductive interface and the first inner electrically conductive interface function  
16 as the cathode electrode. The second porous inner electrolyte layer in combination with the  
17 second metallic layer and its second pattern of perforations, the second inner ionically  
18 conductive interface and the second inner electrically conductive interface function as the anode  
19 electrode. Oxygen gas enters and exits the first porous inner electrolyte layer through the first  
20 pattern of perforations. As the first porous inner electrolyte layer is a mixed conductor,  
21 electrons, oxygen ions and adsorbed oxygen gas can come into intimate contact at many points  
22 throughout its bulk and at both the first inner ionically conductive and the first inner electrically  
23 conductive interfaces. Likewise, hydrogen fuel gas and water vapour enter and exit the second  
24 porous inner electrolyte layer through the second pattern of perforations. As the second porous  
25 inner electrolyte layer is a mixed conductor, electrons, oxygen ions and adsorbed hydrogen fuel  
26 gas can come into intimate contact at many points throughout its bulk and at both the second  
27 inner ionically conductive and the second inner electrically conductive interfaces. Where the  
28 thickness of the central electrolyte membrane and each of the porous inner electrolyte layers is  
29 kept short, each less than about 5  $\mu\text{m}$ , the electrode structures of the present invention provide a  
30 high density of electrochemically active sites in combination with both short ionic and electronic  
31 conductor path length producing both high area specific current density and low internal  
32 resistive losses. In addition to providing a high density of electrochemically active sites the  
33 porous inner electrolyte layers provide the means to accommodate mismatches in thermal

1 coefficients of expansion between the materials used for the ceramic electrolyte layers and the  
2 materials used for the metallic layers.

3 The second embodiment of the invention is shown generally in Fig. 9, and described in  
4 greater detail below, with like reference numerals being used to refer to like features from the  
5 first embodiment of Fig. 1 – Fig. 7.

6 Fig. 9 shows a schematic expanded cross sectional view of a metal-supported solid  
7 electrolyte electrochemical cell operating as a solid oxide fuel cell and incorporating both first  
8 and second porous inner electrolyte layers, a first outer electrolyte layer but no second outer  
9 electrolyte layer. As illustrated, the first porous inner electrolyte layer 31 in combination with  
10 the first metallic layer 3 and its first pattern of perforations 1, the first outer electrolyte layer 4,  
11 the first inner ionically conductive interface 32, the first inner electrically conductive interface  
12 33, the first porous ionically conductive interface 34, and the first electrically conductive  
13 interface 9 function as the cathode electrode. The second porous inner electrolyte layer 41 in  
14 combination with the second metallic layer 5 and its second pattern of perforations 2, the second  
15 inner ionically conductive interface 42 and the second inner electrically conductive interface 43  
16 together function as the anode electrode. On the cathode side, oxygen gas is adsorbed onto the  
17 surface of the outer electrolyte layer 4 and also diffuses into and out of the first porous inner  
18 electrolyte layer 31, through the first pattern of perforations 1 and the first porous ionically  
19 conductive interface 34. As illustrated, hydrogen fuel gas and water vapour diffuse into and out  
20 of the second porous electrolyte layer 41 through the second pattern of perforations 2. The  
21 central electrolyte membrane 7 is designed to be gas impermeable and, since what is illustrated  
22 is a solid oxide fuel cell, to have good oxygen ion conductivity but ideally no electronic  
23 conductivity. To achieve stable and robust ionically conductive pathways through the cell, the  
24 first and second inner ionically conductive interfaces should provide continuous, intimate and  
25 adherent contact between the porous inner electrolyte layers and the central electrolyte  
26 membrane. Likewise, the integrity of the first and second inner electrically conductive  
27 interfaces is critical to achieving reduced electrical resistance for the cell and is a very important  
28 consideration in selecting materials for the first and second metallic layers.

29 It should be noted that while the details shown in Fig. 1a – 7b and associated  
30 descriptions illustrate only metal-supported solid electrolyte electrochemical cells without  
31 porous inner electrolyte layers such details also apply to metal-supported solid electrolyte  
32 electrochemical cells incorporating porous inner electrolyte layers.

33 A range of ceramic electrolyte materials and metallic materials from which the metal-  
34 supported electrochemical cell described herein can be constructed are already known in the art.

1 However, it will be recognized that the cell and multi cell reactor designs described herein can  
2 readily incorporate new and improved electrolyte and metallic materials.

3 Electrolyte Materials

4 The primary considerations in selecting electrolyte materials are that they be stable at the  
5 cell operating conditions and that they achieve the highest possible ionic conductivity at the  
6 lowest operating temperature. As used herein, in reference to electrolyte or metallic materials,  
7 "stability" refers to a material's ability to remain unchanged chemically and/or microstructurally  
8 during cell manufacture and operation, including its ability to resist continued interdiffusion and  
9 reaction with other materials to which it may be bonded and/or contacted, and to resist  
10 undesirable chemical reactions with gaseous atmospheres. For the cells described herein,  
11 operating temperatures are intended to be less than about 800° C and operating temperatures at  
12 or below 650° C are preferred since this lower temperature regime increases the selection and  
13 extends the life of the candidate materials that may be used both for the metallic layers in the  
14 cell itself and for metallic gas manifolds and metallic interconnect elements. Layered  
15 composites of more than one electrolyte material may be used to advantage by, for example,  
16 sandwiching a layer of a more ionically conductive but less stable material between two layers  
17 of a more stable but less ionically conductive material to provide a net increase in ionic  
18 conductivity with no loss in stability. For example, such layered composite electrolytes are  
19 described in US Patent 5,725,965. As used to produce the metal-supported solid electrolyte  
20 electrochemical cells described herein, electrolyte materials are in the form of thin films and/or  
21 coatings. Most preferably these thin films and/or coatings are dense and free of cracks.

22 Generally, any ionically conductive solid may be used as an electrolyte material in the  
23 metal-supported solid electrolyte electrochemical cells described herein. The electrolyte  
24 material may conduct one or more ionic species and each such ionic species may carry either a  
25 positive or negative electrical charge. Examples of such ionic species include oxygen ions ( $O^-$ ),  
26 hydrogen ions ( $H^+$ ) and sodium ions ( $Na^+$ ). Preferred electrolyte materials for the  
27 electrochemical cells described herein are oxygen ion conductors or mixed oxygen ion and  
28 electronic conductors. Minh and Takahashi, *Science and Technology of Ceramic Fuel Cells*,  
29 Elsevier, 1995, chapters 3, 4 and 5, teach useful examples of suitable oxygen ion conducting  
30 electrolyte materials. Representative oxygen ion or mixed oxygen ion and electronic conducting  
31 materials include fully stabilized zirconia, partially stabilized zirconia, doped ceria, doped  
32 bismuth oxide, perovskite oxides such as  $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$  and the like, and  
33 pyrochlore oxides such as  $Gd_2(Zr_{0.6}Ti_{0.4})_2O_7$  and the like. Where the first porous inner  
34 electrolyte layer, and/or the second porous inner electrolyte layer, and/or the first outer

1    electrolyte layer, and/or the second outer electrolyte layer contain predominantly electronically  
2    conductive phases these may comprise electronically conductive ceramics such as mixed metal  
3    oxides or single metal oxides, metals or combinations of electronically conductive ceramics and  
4    metals. Representative electronically conductive materials include perovskite oxides such as  
5     $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$  and  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ , oxides of silver and metals such as platinum, palladium and  
6    silver.

7    Materials for First and Second Metallic Layers

8       There are several important criteria for selecting materials for the first and second  
9    metallic layers. First, the coefficient of thermal expansion of the metallic material must be  
10   matched as closely as possible to that of the chosen electrolyte materials so as to minimize  
11   stresses that might cause the cell to delaminate. The metallic material must exhibit adequate  
12   electrical conductivity through its bulk and in particular at and through its surface especially  
13   where the metallic material inherently includes a surface oxide layer. The metallic material  
14   must provide adequate strength at the intended cell operating temperature. The metallic material  
15   should be stable under the cell operating conditions so as to provide long operating life. Ideally,  
16   the metallic material should also be low cost both from a commodity cost and from a processing  
17   cost standpoint. For the first and second metallic layers, stability primarily refers to the ability  
18   to resist oxidation at the desired operating temperature for the cell. While it is not necessary that  
19   the material selected for the first metallic layer be the same as the material selected for the  
20   second metallic layer, it is preferred that they be the same to simplify the design of the interfaces  
21   between dissimilar materials within the cell.

22      Representative materials for the first and second metallic layers include: nickel, gold,  
23   silver, platinum, chromium, chromium-iron alloys, ferritic stainless steels, austenitic stainless  
24   steels, nickel based super alloys, titanium and titanium alloys. Preferred metallic materials  
25   include chromium-iron alloys, ferritic stainless steels, austenitic stainless steels and nickel based  
26   super alloys. Where stabilized zirconia and/or doped ceria are used as the electrolyte materials,  
27   the most preferred metallic materials include chromium-iron alloys and ferritic stainless steels.  
28   As more generally determined from a cost standpoint, the most preferred materials include  
29   ferritic stainless steels and austenitic stainless steels.

30      As used to produce the first and/or second metallic layer described herein, metallic  
31   materials may be in the form of wrought foils, thin films, coatings and/or combinations of the  
32   foregoing. Metallic layers in the form of thin films or coatings may be produced by a range of  
33   coating processes including sputtering, chemical vapour deposition, electroless plating, electro  
34   plating, screen printing plus sintering, slurry coating plus sintering and tape lamination plus

1 sintering. Preferably a wrought foil comprises the major part of at least one of the first metallic  
2 layer or the second metallic layer. Most preferably a wrought foil comprises the major part of  
3 both the first and second metallic layers.

4 Materials for the Metallic Interconnect Elements

5 The criteria for selecting materials for the metallic interconnect elements are similar to  
6 the criteria already described for selecting materials for the first and second metallic layers.  
7 However, for the metallic interconnect elements 12, the requirement to closely match the  
8 coefficient of thermal expansion to that of the electrolytes used is relaxed. Also, the material of  
9 the metallic interconnect elements must be compatible with the material of the first and second  
10 metallic layers with respect to the metallurgical bonding techniques used to join these materials.  
11 Representative materials for the metallic interconnect elements include: nickel, gold, silver,  
12 platinum, chromium-iron alloys, ferritic stainless steels, austenitic stainless steels, nickel based  
13 super alloys, titanium and titanium alloys. Preferred materials include ferritic stainless steels,  
14 austenitic stainless steels and nickel based super alloys.

15 As used to produce the metallic interconnect elements 12 described herein, metallic  
16 materials may be in the form of wrought foils, wrought thin sheets, wrought thin strip, castings  
17 and/or combinations of the foregoing. The preferred forms are wrought foils and/or wrought  
18 thin sheets.

19 Thickness Considerations

20 The central electrolyte membrane is preferably made as thin as possible to reduce  
21 stresses that tend to cause the cell to delaminate as a consequence of mismatches between the  
22 thermal expansion coefficient of the central electrolyte membrane and the thermal expansion  
23 coefficient of the first and/or second metallic layers. It is also desirable in certain arrangements  
24 of the first and second pattern of perforations to make the central electrolyte membrane as thin  
25 as possible to achieve the shortest possible ionic conductor path from one side of the membrane  
26 to the other. On the other hand, it is more difficult to achieve reliable electrical isolation  
27 between the first and second metallic layers when the central electrolyte membrane is less than  
28 about 0.5  $\mu\text{m}$  thick. This is especially the case where the surface roughness of the first and/or  
29 second metallic layers, on those surfaces to which the central electrolyte membrane is adhered,  
30 is of the same magnitude as the thickness of the central electrolyte membrane. The thickness of  
31 the central electrolyte membrane is also dependent on the characteristics of the manufacturing  
32 process by which it is made. For example, if the central electrolyte membrane is formed by  
33 sputtering a film of the electrolyte material onto one of the metallic layers then it becomes more

1 difficult to manage residual stresses in this electrolyte film as the thickness of the film increases  
2 beyond about 1 micron. Considering the foregoing factors, the thickness of the central  
3 electrolyte membrane preferably ranges from about 0.5  $\mu\text{m}$  to about 10  $\mu\text{m}$  and most preferably  
4 ranges from about 0.8  $\mu\text{m}$  to about 5  $\mu\text{m}$ .

5 The first and second porous inner electrolyte layers are preferably as thin as possible in  
6 order to provide the shortest possible ionic conductor pathway through the cell. At the same  
7 time, these porous layers should be thick enough to provide adequately large gas flow pathways  
8 throughout their bulk to permit unrestricted flow of the reacting gases. Considering these  
9 factors the thickness of the first and/or second porous inner electrolyte layers ranges from about  
10 0.5  $\mu\text{m}$  to about 10  $\mu\text{m}$  and more preferably ranges from about 1 micron to about 5  $\mu\text{m}$ .

11 At least one of the first metallic layer and the second metallic layer provides the  
12 mechanical support for the cell, i.e., one of these layers must be the supporting metallic layer,  
13 and is typically at least 2 times, and preferably at least 4 times, thicker than the central  
14 electrolyte membrane, such that the complete cell structure behaves mechanically as though it  
15 were made entirely of metal. The desire to achieve a mechanically more robust cell, unless  
16 achieved by providing more bonding points to a stiff metallic interconnect element, also requires  
17 that the thickness of at least one of the first or second metallic layers be increased. It is also  
18 easier to achieve satisfactory metallurgical bonds between the first and or second metallic layers  
19 and the metallic interconnect elements when the thickness of the first and second metallic layers  
20 is greater than about 10  $\mu\text{m}$ . The desire to reduce electronic resistance in the cell, which is  
21 important in solid oxide fuel cell applications, also calls for thicker metallic layers, but in this  
22 case both metallic layers are thicker. Electronic resistance in the metallic layers is determined  
23 by the spacing between electrical connections to the metallic interconnect elements and by the  
24 thickness and electronic conductivity of the first and second inner electrically conductive  
25 interfaces and/or the first and second electrically conductive interfaces. From the standpoint of  
26 electrical resistance in the cell, it is desirable that the electrically conductive interfaces be as thin  
27 as possible. On the other hand, it is much easier to provide a high density of perforations,  
28 resulting in better electrode gas flow performance and/or shorter average ionic conductor path  
29 length and increased current density for the cell, if both the first and second metallic layers are  
30 kept as thin as possible. Considering the foregoing factors, the thickness of the first metallic  
31 layer and the second metallic layer preferably ranges from about 5  $\mu\text{m}$  to about 75  $\mu\text{m}$  and most  
32 preferably ranges from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ .

1 To minimize ionic resistance in the cell that does not incorporate porous inner electrolyte  
2 layers it is desirable to increase the thickness of both the first and second outer electrolyte layers  
3 as this provides an increased ionic conductor cross sectional area. This is especially important  
4 where the density of the patterns of perforations through the first and second metallic layers is  
5 reduced, as can result when these metallic layers are thicker than about 30  $\mu\text{m}$ . It is also  
6 desirable that the outer electrolyte layers be thicker to provide increased protection to the  
7 underlying metallic layers against attack by the operating atmospheres in the cell. On the other  
8 hand, it is desirable to keep the outer electrolyte layers as thin as possible to minimize the  
9 delamination stresses that could cause them to spall off. Considering the foregoing factors, the  
10 thickness of the first and second outer electrolyte layers preferably ranges from about 0.1  $\mu\text{m}$  to  
11 about 4  $\mu\text{m}$  and most preferably ranges from about 0.2  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

12 Referring to Fig. 7, it can be seen that the total thickness of the metallic interconnect  
13 element is made up of the sum of the height of the bumps or ribs on the top side of the element,  
14 dimension H1, the height of the bumps or ribs on the bottom side of the element, dimension H2,  
15 and the thickness of the metallic sheet from which the element is made, dimension T.  
16 Dimensions H1 and H2 are determined in relation to the size of gas flow channel required to  
17 handle the design gas flows to and from the cell electrode surfaces, which is directly  
18 proportional to the width of the active cell area, dimension H, and by whether or not a stiff  
19 porous support material is inserted into the gas flow channels to provide additional support to  
20 the electrochemical cells. H1 and H2 need not be the same, although it is desirable for  
21 simplicity that they be so. Typically, H1 and H2 range from about 0.2 mm to about 3 mm and  
22 preferably range from about 0.2 mm to about 1 mm. Typically, T ranges from about 0.1 mm to  
23 about 2 mm and preferably from about 0.1 mm to about 1 mm. Therefore, the overall thickness  
24 of the metallic interconnect elements typically ranges from about 0.5 mm to about 8 mm and  
25 preferably ranges from about 0.5 mm to about 3 mm.

26 Pattern of Perforations

27 The functions of the first and second pattern of perforations are to provide gas access to  
28 the porous inner electrolyte layers, or to expose the central electrolyte membrane such that the  
29 outer electrolyte layers make intimate contact with the central electrolyte membrane, and thus  
30 complete an ionic conductor path through the cell (i.e., from one side of the central electrolyte  
31 membrane to the other). The individual perforations may be of any size and shape providing  
32 that adequate structural support is provided to the central electrolyte membrane by the first  
33 and/or second metallic layers and that the metallic layers, incorporating the perforations, have  
34 sufficiently large metallic conductor pathways to provide low electrical resistance to the cell.

1 The arrangement of the patterns, including the density of perforations per unit area of cell  
2 surface, may be varied from one area to another over the surface of the first and/or second  
3 metallic layers. The first pattern of perforations may be the same as or different from the second  
4 pattern of perforations. To maximize electrode gas flow performance and/or to minimize ionic  
5 conductor path lengths and thus maximize ionic current through the cell, the size of individual  
6 perforations should be small, and the density of perforations per unit area of cell surface, on  
7 both the first and second metallic layers, should be as high as possible. The side walls of the  
8 individual perforations are preferably, but not necessarily, approximately perpendicular to the  
9 surface of the central electrolyte membrane since this permits a greater density of perforations  
10 per unit of surface area and provides larger, lower resistance electronic conductor paths for a  
11 given perforation shape and pattern density.

12 **Representative Manufacturing Processes**

13 Fig. 8 is a flow chart of a representative manufacturing process to produce a reactor  
14 incorporating multiple metal-supported solid electrolyte electrochemical cells of the first  
15 embodiment of this invention, which cells do not incorporate porous inner electrolyte layers.  
16 Process operations shown on the left side of the page apply to producing the second metallic  
17 layer, the second pattern of perforations, the second outer electrolyte layer and the second  
18 ionically conductive interface. The process operation that produces the central electrolyte  
19 membrane is also shown on the left side of the page. Process operations shown on the right side  
20 of the page apply to producing the first metallic layer, the first pattern of perforations, the first  
21 outer electrolyte layer and the first ionically conductive interface. Process operations shown  
22 centred on the vertical centre of the page apply to the whole cell or to the whole reactor  
23 assembly. Process operations shown above the horizontal broken line at Z-Z apply to individual  
24 cell production and those operations shown below the line Z-Z apply to multi cell reactor  
25 production. It is clear from Fig. 8 is that the production of individual cells involves a number of  
26 sequential lamination, coating or film-forming process operations that build up a five-layered  
27 laminated structure interspersed with process operations to remove metallic material to form the  
28 perforation patterns. The overall manufacturing process is similar to the overall manufacturing  
29 processes used in the electronics industry to produce double sided printed circuit boards and in  
30 particular to produce double-sided flexible printed circuits.

31 The metallic layers may be provided, as is shown in Fig. 8, as wrought foils and this is  
32 preferred as it permits ready control over the composition and mechanical properties of the  
33 metallic materials. However, if both metallic layers are formed from wrought foils a process  
34 must be provided to laminate at least one of the metallic layers to the ceramic central electrolyte

1 membrane. Also, a process must be provided to remove material from the foils to produce the  
2 patterns of perforations. Representative processes to provide the pattern of perforations include  
3 a range of photolithographic and chemical etching processes such as those used to produce  
4 printed circuit boards or, more particularly, such as those used in the photochemical machining  
5 industry to produce miniature components from stainless steel materials. These same patterning  
6 or photochemical machining processes may also be used in the manufacture of the metallic  
7 interconnect elements. A preferred process which provides that both the first and second  
8 metallic layers are provided as wrought foils is summarized in Fig.8, wherein one foil is first  
9 provided with an appropriate pattern of perforations while the other is coated with a pre-fired  
10 "loaded sol-gel" coating of the electrolyte material that will form the central electrolyte  
11 membrane. The two foils are then pressed together such that the continuous foil and the  
12 perforated foil sandwich the pre-fired "loaded sol-gel" electrolyte coating. Upon firing the  
13 "loaded so-gel" coating densifies and bonds to both the continuous foil and to the perforated  
14 foil. The perforations in the perforated foil provide a means of escape for the volatile organics  
15 that evolve during firing of the "loaded sol-gel" coating. A suitable "loaded sol-gel" coating  
16 process is described in US Patent 5,585,136. Alternatively, a multi layered combination of a  
17 "loaded sol-gel" and a (conventional) sol-gel process may be used. Representative sol-gel  
18 processes are described in US Patent 5,494,700.

19 Alternatively, the first and/or the second metallic layers may be produced by either  
20 single or multiple coating and/or plating processes. The principal disadvantage of this approach  
21 is that the degree of control over the composition and mechanical properties of the metallic  
22 layers is reduced. The advantages of this approach are that: the pattern of perforations may be  
23 formed as the metallic layers themselves are produced, thus eliminating the need for a separate  
24 patterning process; a high density of perforations is achievable even where the metallic layer is  
25 thicker than 10  $\mu\text{m}$ ; and the side-walls of individual perforations can be made approximately  
26 perpendicular to the surface of the central electrolyte membrane. Representative processes  
27 include electroless plating, electroplating of metals and alloys, DC magnetron sputtering of  
28 metals and alloys, and combinations thereof. A representative process to produce densely  
29 packed steep-walled vias or perforations in tick metal layers is described in Leith and Schwartz,  
30 High-Rate Through-Mold Electrodeposition of Thick (>200  $\mu\text{m}$ ) NiFe MEMS Components  
31 with Uniform Composition, Journal of Microelectromechanical Systems, Vol. 8, No.4,  
32 December 1999. The first and/or second metallic layer may also be provided by a range of  
33 processes that involve applying the metal or alloy as a powder, typically held in a polymeric  
34 binder, and subsequently sintering the powder to produce a dense monolithic metallic layer.

1 Representative processes for providing the pre-sintered metallic layer are screen printing, slurry  
2 coating and tape casting/lamination.

3 In addition to the sol-gel and “loaded sol-gel” coating processes already referenced  
4 herein, the central electrolyte membrane and the outer electrolyte layers may be produced by  
5 any process that produces a satisfactory ceramic coating. Representative coating processes  
6 include reactive DC magnetron sputtering, RF magnetron sputtering and chemical vapour  
7 deposition. For example, representative DC and RF magnetron sputtering processes for  
8 depositing layers of yttria stabilized zirconia, a preferred electrolyte material for solid oxide fuel  
9 cells, are described in US Patent 5,753,385. Preferred processes for forming the central  
10 electrolyte membrane are by providing single layer or multi layer coatings by the “loaded sol-  
11 gel” process, already referenced herein, or by providing multi layer coatings that combine  
12 “loaded sol-gel” and sol-gel coatings. Preferred coating processes for forming the outer  
13 electrolyte layers include “loaded sol-gel,” sol-gel, polarized electrochemical vapour deposition  
14 (PEVD) and combinations thereof. The most preferred process to produce the outer electrolyte  
15 layers is to first apply a single or multi layer sol-gel coating followed by a PEVD coating. The  
16 PEVD process is described in Tang et al, A New Vapor Deposition Method to Form Composite  
17 Anodes for Solid Oxide Fuel Cells, Journal of the American Ceramics Society, 83[7] 1626-32  
18 (2000). The advantage of the PEVD process is that it produces robust ionically conductive  
19 interfaces between the central electrolyte membrane and the outer electrolyte layers and also  
20 fills in cracks in the outer electrolyte layers, thus providing a robust ionic conductor path  
21 through the cell.

22 Fig. 10 is a flow chart of a representative manufacturing process to produce a reactor  
23 incorporating multiple metal-supported solid electrolyte electrochemical cells of the second  
24 embodiment of the invention, which cells incorporate porous inner electrolyte layers and a first  
25 outer electrolyte layer, but do not incorporate a second outer electrolyte layer. It should be  
26 noted that the inclusion of a first outer electrolyte layer and omission of a second outer  
27 electrolyte layer is done simply to illustrate that either or bot of these layers may be readily  
28 added or deleted from the overall manufacturing process. Process operations shown on the left  
29 side of the page apply to producing the second metallic layer, the second pattern of perforations,  
30 the second porous inner electrolyte layer and the second inner ionically conductive interface.  
31 Process operations shown on the right side of the page apply to producing the first metallic  
32 layer, the first pattern of perforations, the first porous inner electrolyte layer, the first outer  
33 electrolyte layer and the first inner ionically conductive interface. Process operations shown  
34 centred on the vertical centre of the page apply to production of the central electrolyte

1 membrane for individual cells and of the whole reactor assembly. Process operations shown  
2 above the horizontal broken line at Z-Z apply to individual cell production and those operations  
3 shown below the line Z-Z apply to multi cell reactor production. The PEVD coating operations,  
4 of which the principal purpose is to strengthen the inner ionically conductive interfaces, are  
5 included to illustrate that they may be part of the overall manufacturing process if required.  
6 However, for cost minimization purposes it is desired and, particularly in the case of metal-  
7 supported solid electrolyte cells that incorporate porous inner electrolyte layers, expected that  
8 the PEVD process operations will not be required.

9 It is clear that the overall manufacturing process and individual process operations  
10 shown in Fig. 10 are the same as those shown in Fig. 8 with the exception of specific process  
11 operations required to produce the porous inner electrolyte layers. The porous inner electrolyte  
12 layers may be produced by any process that produces a suitable porous ceramic coating.  
13 Representative processes include suitably adapted tape casting and lamination, screen printing,  
14 reactive DC and RF sputtering, sol-gel, and "filled sol-gel" processes. A representative and  
15 broadly applicable adaptation used to achieve and/or enhance the porosity of coatings involves  
16 the inclusion a fugitive pore-forming filler material that is typically removed by a burn-out or  
17 leaching operation after the coating is formed. The "filled sol-gel" process already described  
18 herein lends itself very well to the production of porous multi phase ceramic electrolyte coatings  
19 and is a preferred method for manufacturing the porous inner electrolyte layers of the metal-  
20 supported solid electrolyte electrochemical cells described herein.

21 **Modified Electrically Conductive Interfaces**

22 In another embodiment of the metal-supported solid electrolyte electrochemical cell  
23 described herein, the first inner electrically conductive interface and/or the second inner  
24 electrically interface and/or the first electrically conductive interface and/or the second  
25 electrically conductive interface is modified, by the addition of particular metal layers, such that  
26 particular metal oxide compositions are formed that increase the electrical conductivity of the  
27 electrically conductive interface above what it would otherwise be and/or render it more stable  
28 at the cell operating conditions. Representative materials that may be used to increase the  
29 conductivity of the first and second inner electrically conductive interfaces and/or the first and  
30 second electrically conductive interfaces depend on the specific materials selected for the first  
31 and second metallic layers. Where the metallic layers are of a chromium rich alloy that forms a  
32 chromium oxide scale, representative metals such as manganese, magnesium and zinc may be  
33 incorporated to produce a modified surface oxide scale exhibiting increased electrical  
34 conductivity and stability. Manganese is a preferred material for use with chromium rich alloys.

1 US Patent 6,054,231 describes suitable materials and processes for providing such a modified  
2 electrically conductive surface layer on chromium rich alloys for use on the anode facing side of  
3 metallic bipolar interconnect elements in solid oxide fuel cells. Such chromium rich alloys are  
4 also preferred materials for the first and second metallic layers of the metal-supported solid  
5 electrolyte electrochemical cells described herein. It is worth noting that the desired surface  
6 oxides may also be obtained by adding a sufficient concentration of the desired surface oxide  
7 modifying metal to the formulation of the alloy from which the first and/or second metallic  
8 layers are made. For example, 5% by weight or more of manganese might be added to a ferritic  
9 stainless steel. However, such changes to alloy formulation can change the thermal expansion  
10 characteristics quite markedly such that the alloy no longer presents a good match to the thermal  
11 expansion characteristic of the chosen electrolyte materials.

12 Metallurgically Bonded Gas Seals and/or Electrical Interconnects

13 In another preferred embodiment, the first metallic layer and the second metallic layer of  
14 the metal-supported solid electrolyte electrochemical cell are each metallurgically bonded to one  
15 or more metallic interconnect elements. As used herein, the terms "metallurgically bonding" or  
16 "metallurgically bonded" means joined by a welding or brazing process, and the term  
17 "metallurgical bond" means the joint formed by metallurgical bonding. The metallurgical  
18 bonding of the first and second metallic layers to the metallic interconnect elements may occur  
19 only at the cell periphery. Alternatively, to provide greater mechanical strength and/or lower  
20 electrical resistance to the cell, the first and second metallic layers may also be metallurgically  
21 bonded to the metallic interconnect elements at many points across their surface where these  
22 bonding points are arranged to minimize restrictions in the flow of gas to and from the electrode  
23 surfaces.

24 Fig. 3a, 3b show a plan view and a sectional view of a representative schematic for a  
25 multi cell reactor incorporating metal-supported solid electrolyte electrochemical cells and  
26 metallic interconnect elements, which interconnect elements provide both series electrical  
27 interconnection between the stacked cells and gas flow channels to transport the relevant gases  
28 to and from the electrode surfaces. The peripheral gas seals and electrical interconnects 13  
29 and/or the interior interconnects 14 between the first metallic layer 3 and/or the second metallic  
30 layer 5 and the metallic interconnect elements 12 may be made by metallurgically bonding the  
31 first metallic layer 3 and/or the second metallic layer 5 to the metallic interconnect element 12.  
32 Fig. 4a, 4b show a detailed cross sectional view for the case where the peripheral gas seal and  
33 interconnect 13 is metallurgically bonded by a brazing technique and incorporates the braze  
34 filler metal 17. The central electrolyte membrane 7 preserves electrical isolation between the

1 first metallic layer 3 and the second metallic layer 5 in making such a metallurgically bonded  
2 interconnect. Since this is easier to achieve by brazing than by welding techniques, brazing is  
3 the preferred metallurgical bonding process. The first pattern of perforations 1 and/or the  
4 second pattern of perforations 2 may extend under the braze filler metal since the width of the  
5 braze joint spans over many perforations and thus provides a reliable gas seal and/or electrical  
6 interconnections. While the metal-supported solid electrolyte electrochemical cells shown in  
7 Fig. 4a, 4b do not incorporate porous inner electrolyte layers, it should be understood that the  
8 metallurgical bonding details illustrated in Fig. 4a, 4b also apply to metal-supported solid  
9 electrolyte electrochemical cells incorporating such porous inner electrolyte layers.

10 Any metallurgical bonding process that results in the formation of a satisfactory metallic  
11 bond between the first and/or second metallic layers and the metallic interconnect elements may  
12 be used. The selection of the bonding process depends on the selection of the materials for the  
13 first and second metallic layers and for the metallic interconnect elements. In general, suitable  
14 metallurgical bonding processes include a variety of brazing and welding techniques, and  
15 combinations thereof. For many of the candidate metallic materials that may be used to build  
16 metal-supported solid electrolyte electrochemical cells, suitable metallurgical bonding processes  
17 are already practiced widely. For example, several welding and brazing processes for joining  
18 stainless steels, nickel alloys, titanium alloys and chromium-iron alloys are in widespread  
19 commercial use and these same processes can be used in the building of the metal-supported  
20 cells described herein. The preferred metallurgical bonding processes are vacuum brazing, inert  
21 atmosphere brazing, resistance welding and combinations thereof. The most preferred  
22 metallurgical bonding processes are vacuum brazing and/or inert atmosphere brazing because  
23 these processes provide minimal damage to the central electrolyte membrane of the cell, and  
24 provide a ready means to make metallurgical bonds at internal mating surfaces after the cells  
25 and metallic interconnect elements have been assembled, but not yet metallurgically bonded,  
26 into a multi cell reactor. For multi cell reactor assembly, braze filler metal may conveniently be  
27 provided to those areas to be metallurgically bonded in the form of preformed tapes, wire  
28 gaskets, foil gaskets, pastes or combinations of the foregoing.

29 Outer Electrolyte Over Metallurgical Bond

30 In another embodiment of the solid electrolyte electrochemical cell described herein, the  
31 first outer electrolyte layer and/or the second outer electrolyte layer extend over the area where  
32 the metallurgical bond occurs between the first and/or second metallic layers and the adjacent  
33 metallic interconnect elements. The outer electrolyte layers may also extend over all or a part of  
34 the surface of the metallic interconnect elements. The outer electrolyte layer, which is itself

selected to be a stable ceramic, thus provides protection to all underlying metal surfaces that would otherwise be directly exposed to the cell's operating atmospheres. For example, the outer electrolyte layer can protect underlying metallic materials from oxidation, carburization and/or attack by sulphur compounds such as hydrogen sulphide gas. The preferred method for extending the outer electrolyte layers over the metallurgical bonding area is by the PEVD process already referenced herein as this is a modified chemical vapour deposition/coating process and can be carried out after the cell has been assembled into a multi cell reactor. The PEVD process is effective for this purpose since the bonding surface and any other metallic surface to be coated with the outer electrolyte layer are electronically conductive. The preferred process for extending the outer electrolyte layer over the surface of the metallic interconnect elements is to first apply a coating of the outer electrolyte material to the metallic interconnect elements on all surfaces, except those to be bonded to the first and/or second metallic layers of the cell, then to metallurgically bond the interconnect elements to the first and/or second metallic layers, and finally to complete the outer electrolyte layer by the PEVD process already described. The preferred method for applying the electrolyte coating to the metallic interconnect elements is by the sol-gel or loaded sol-gel techniques already described but any other method of applying ceramic coatings to dense metallic surfaces may also be used. This coating may have cracks and other minor discontinuities as these can be filled in by the subsequent PEVD coating process.

Fig. 4b, Detail C from Fig. 3b shows a metallurgically bonded gas seal and interconnect at the periphery of a metal-supported cell. It can be seen that both the first outer electrolyte layer 4 and the second outer electrolyte layer 6 extent over the metallurgical bonds 17 and those areas of the metallic interconnect elements 12 immediately adjacent to the metallurgical bonds 17.

#### 25 Pattern of Perforations to Yield Robust Gas Impermeable Membrane

In another embodiment of the metal-supported solid electrolyte electrochemical cell described herein, the first pattern of perforations and the second pattern of perforations are so arranged such that the central solid electrolyte membrane or the laminated structure including the first porous inner electrolyte layer, the central electrolyte membrane and the second porous inner electrolyte, hereinafter referred to as the inner electrolyte sandwich, is everywhere supported directly by either the first metallic layer and/or the second metallic layer, providing a robust gas impermeable membrane. Fig. 1a, 1b show such an arrangement of the first and second pattern of perforations where it can be seen that the central membrane 7 is everywhere in contact with and supported by either the first metallic layer 3 or the second metallic layer 5.

1 Where the metallic layers are made relatively thick, preferably more than about 20 $\mu\text{m}$ , and/or  
2 where the first and/or second metallic layers are metallurgically bonded to robust metallic  
3 interconnect elements at frequent intervals, preferable spaced at about 1.5 cm or less, then the  
4 cell is capable of withstanding significant differentials in pressure between one side and the  
5 other. Alternatively, the cell may be supported mechanically, at least on the low pressure side of  
6 the membrane, by being brought into contact with a stiff, gas permeable, perforated or porous or  
7 mesh-like metallic, ceramic or metal/ceramic composite element over its entire area. Such  
8 metal-supported cells with robust gas impermeable electrolyte membranes are particularly  
9 useful in electrically driven oxygen concentration reactors and in pressure driven partial  
10 oxidation reactors.

11 Pattern of Perforations to Yield Short Ionic Path

12 In another embodiment of the metal-supported solid electrolyte electrochemical cell not  
13 incorporating porous inner electrolyte layers described herein, the first pattern of perforations  
14 and the second pattern of perforations are arranged so as to define areas where the central solid  
15 electrolyte membrane is supported directly by neither the first metallic layer nor the second  
16 metallic layer, thus providing at these areas an ionic conduction path between each side of the  
17 cell that is defined only by the thickness of the central solid electrolyte membrane. By this  
18 approach it is possible to achieve ionic conductor path lengths of only a few  $\mu\text{m}$  which  
19 facilitates lower operating temperatures, increased current densities or both. Fig. 5a, 5b show an  
20 example of such an arrangement of the first and second pattern of perforations where the  
21 perforations in both the first metallic layer 3 and the second metallic layer 5 are elongated in  
22 shape, for example where their length is about 5 times their breadth, and at the same time the  
23 first pattern of perforations 1 and the second pattern of perforations 2 are deliberately arranged to  
24 be non-parallel thus defining areas where the central electrolyte membrane is not supported  
25 where the patterns overlap. Such an arrangement also greatly simplifies the task of aligning the  
26 first pattern of perforations and the second pattern of perforations which is very advantageous  
27 from a manufacturing standpoint.

28 Pattern of Perforations to Achieve Reduced Thermal Gradients in Individual Cells

29 In another embodiment of the metal-supported solid electrolyte electrochemical cell  
30 described herein, the first pattern of perforations and/or the second pattern of perforations are  
31 arranged so as to vary the electrochemical current density areally over the surface of the  
32 electrodes by varying the density of perforations from one area to another over the surface of the  
33 cell, as for example from the center to the edge. Thereby it is possible to reduce temperature

1 gradients in the cell associated with areal variations in the concentration and/or the temperature  
2 of the reacting gasses over the electrode surfaces. In this manner it is possible to tailor the  
3 design of individual cells to match/compensate for the gas flow patterns associated with  
4 particular reactor designs.

5 Specialized Catalysts on the Electrodes

6 In another embodiment of the metal-supported solid electrolyte electrochemical cell  
7 described herein, specialized catalysts are incorporated onto or into the first porous inner  
8 electrolyte layer and/or the second porous inner electrolyte layer and/or the first outer electrolyte  
9 layer and/or the second outer electrolyte layer. For example, such catalysts may be selected to  
10 enhance certain preferred fuel gas reforming in a solid oxide fuel cell or particular oxidation  
11 reactions in a partial oxidation reactor. The catalyst must be present at those surfaces of the  
12 porous inner electrolyte layers and/or of the outer electrolyte layers that contact the reacting  
13 gases and must be present in such concentration that it provides the desired catalytic effect but  
14 does not crowd out or otherwise impair the cell's electrochemical reactions. These catalysts  
15 may be applied as very thin discontinuous metal and/or metallic oxide coatings on the surface of  
16 the outer electrolyte layers by such processes as RF or DC magnetron sputtering or chemical  
17 vapour deposition. The preferred approach is to incorporate the catalyst as a very finely  
18 dispersed oxide within the porous inner electrolyte layers and/or the outer electrolyte layers at  
19 the same time as these layers themselves are formed by the sol-gel and/or loaded sol-gel  
20 techniques already referenced herein. Suitable catalyst materials are well known in the art and  
21 include metals and oxides of metals selected from Groups II, V, VI, VII, VIII, IX, X, XI, XV  
22 and the F Block lanthanides of the Periodic Table of elements according to the International  
23 Union of Pure and Applied Chemistry. Particularly suitable materials include metals platinum,  
24 palladium, ruthenium, rhodium, gold, silver, bismuth, cerium, barium, vanadium, nickel, cobalt,  
25 manganese, molybdenum and praseodymium, and/or the oxides of these metals.

26 Preferred Reactor Design

27 In another embodiment, a preferred design for a multi cell reactor incorporating multiple  
28 metal-supported solid electrolyte electrochemical cells is provided. Such a reactor can be used  
29 as a solid oxide fuel cell stack, an oxygen concentration reactor or a partial oxidation reactor. A  
30 schematic layout for such a reactor is presented in Fig. 6a, 6b and 6c where in sectional views  
31 A-A (Fig. 6b) and B-B (Fig. 6c) individual cells 18, each incorporating a first outer electrolyte  
32 layer, a first pattern of perforations, a first electrically conductive interface, a first metallic layer,  
33 a first ionically conductive interface, a central electrolyte membrane, a second ionically  
34 conductive interface, a second metallic layer, a second pattern of perforations, a second

1 electrically conductive interface and a second outer electrolyte layer, are connected in electrical  
2 series by metallic interconnect elements 12. Alternatively, the individual metal-supported cells  
3 18 may each be comprised of a first metallic layer, a first pattern of perforations, a first inner  
4 electrically conductive interface, a first porous inner electrolyte layer, a first inner ionically conductive  
5 interface, a central electrolyte membrane, a second inner ionically conductive interface, a second porous inner electrolyte layer, a second inner electrically conductive interface, a second metallic layer and a second pattern of perforations and may or may not also  
6 incorporate a first porous ionically conductive interface and a first outer electrolyte layer and/or  
7 a second porous ionically conductive interface and a second outer electrolyte layer. The  
8 arrangement of the metal-supported cells 18, the metallic interconnect elements 12 and the  
9 peripheral gas seals and interconnects 13 is as previously described herein. It is preferred that at  
10 least the peripheral gas seals and interconnects 13 and alternatively any interior interconnects as  
11 well be metallurgically bonded.

14 The primary objective and feature of this reactor design is that it is readily scaleable, in  
15 that the active area of individual cells and/or the number of cells in the reactor can be increased  
16 without requiring changes to the dimensions or materials in the active area of the individual  
17 cells, which dimensions and materials govern the electrochemical performance of the cells. This  
18 is achieved in the rectangular cells shown in Fig. 6a by setting and holding constant the width of  
19 the active area of the cells, dimension H, which permits such parameters as the thickness of the  
20 first and second metallic layers, the design of the first and second pattern of perforations, the  
21 size and shape of individual perforations, the thickness of the central electrolyte membrane, the  
22 overall height of the metallic interconnect elements, the layout of the dimpled or ribbed pattern  
23 for the interconnect elements, and the gas flow communication between the manifolds and gas  
24 flow channels to be determined once and thereafter to be held constant. If the number of cells in  
25 the stack is increased then only dimensions B and D need to be increased to provide for enlarged  
26 gas manifolds 16 while all other dimensions remain unchanged. Likewise if the active area of  
27 the individual cells is expanded by expanding dimension L, all other dimension remain  
28 unchanged. It should be noted that ready expansion of dimension L is enabled by the metal-like  
29 mechanical characteristics of the metal-supported cells described herein and that such an  
30 expansion in dimension L would be very difficult to achieve using conventional solid electrolyte  
31 electrochemical cell designs since these exhibit ceramic-like mechanical characteristics. From a  
32 commercial standpoint, scaleability is a very important attribute as it permits the same basic cell  
33 design to be used in a broad range of different products, requiring reactors ranging widely in  
34 size, thus permitting more rapid progress towards large-volume, low-cost manufacturing for the

1 reactors and at the same time providing for continued technical optimization of the basic cell  
2 design.

3 Preferably the dimension H ranges from about 10 mm to about 500 mm and most  
4 preferable ranges from about 20 mm to about 300 mm. Preferably dimension L ranges from  
5 about 50 mm to about 1,000 mm and most preferably ranges from about 100 mm to about  
6 700 mm. Preferably the number of individual cells in the reactor ranges from about 10 to about  
7 500 and most preferably ranges from about 20 to about 200.

8 While a counter flow gas manifolding arrangement as shown in Fig. 6a-6c is preferred,  
9 because it permits the gas supply manifolds to be interspersed with the gas exhaust manifolds  
10 thus providing for more effective preheating of the incoming gasses, the design may also be  
11 configured for a co-flow gas manifolding arrangement.

12 Optionally, the reactor may be provided with liquid heat transfer fluid channels 19 that  
13 run vertically through the height of the reactor and are located adjacent to the gas manifolds 16.  
14 Liquid heat transfer fluid is supplied from the reactor header block 24 and flows vertically down  
15 through the reactor and exits the reactor by the liquid heat transfer fluid return header 20. To  
16 maintain electrical isolation between the first metallic layer and the second metallic layer of the  
17 individual cells in the stack the liquid heat transfer fluid must not be an electrical conductor.

18 The reactor is also provided with a bottom end plate 21, a top section adaptor 22 and a  
19 reactor header block 24. The reactor header block 24 interconnects the vertical gas manifolds  
20 16 and the vertical liquid heat transfer fluid channels 19 to supply and/or return headers that are  
21 external to the reactor. All such external supply and return headers are provided with electrical  
22 isolators to ensure that the only electrical connections to the reactor are by the bottom electrical  
23 terminal 23 and the top electrical terminal 25.

## 24 EXAMPLES

### 25 Example 1

26 A sheet of Haynes Alloy 230 2B annealed foil, 50  $\mu\text{m}$  (0.002 inches) in thickness and  
27 obtained from Elgiloy Speciality Metals of Elgin, Illinois, was coated with an approximately  
28 5  $\mu\text{m}$  thick yttria stabilized zirconia coating by a "loaded" sol-gel coating technique at Datec  
29 Coating Corporation of Milton, Ontario. The finished "loaded" sol-gel coating consisted of  
30 approximately 1  $\mu\text{m}$  sized particles of yttria stabilized zirconia encapsulated in a continuous  
31 matrix of a yttria stabilized zirconia sol-gel coating. The 5  $\mu\text{m}$  thick coating was applied in two  
32 layers, each about 2.5  $\mu\text{m}$  thick. The layers were sprayed on wet and heat treated at less than  
33 600° C for about 10 minutes to crystalize the zirconia sol. This coated nickel based super alloy

1 structure was thermally cycled by heating to 650° C in air in a furnace and quenching to room  
2 temperature by rapid removal from the furnace. The laminate was cool to the touch within 5  
3 seconds of removal from the furnace. The structure survived 5 cycles without evidence of  
4 delamination.

5 Example 2

6 A piece of wrought Grade 430 stainless steel, cold roll temper, having a thickness of  
7 25  $\mu\text{m}$ , obtained from Hamilton Precision Metals Inc. of Lancaster PA and approximately  
8 5 cm x 9 cm in area, was prepared by heat treating in air at 550° C for 30 minutes. A "loaded"  
9 sol-gel coating approximately 5  $\mu\text{m}$  in thickness was applied to one side of the stainless steel  
10 foil as in Example 1. This structure demonstrated excellent adhesion when tested using a tape  
11 adhesion test consisting of applying transparent tape and removing by pulling at 90 degrees.  
12 The sample was thermally cycled, as described in Example 1, for 10 cycles without evidence of  
13 delamination. The sample was cool to the touch within 3 seconds of removal from the furnace  
14 confirming that its low thermal mass offered the potential to rapidly bring it to the target  
15 operating temperature for a solid oxide electrolyte based electrochemical cell. The tape  
16 adhesion test was repeated after the thermal cycling tests and again excellent adhesion of the  
17 "filled" sol-gel coating was observed. SEM images indicated that the coating contained micron-  
18 sized interconnected porosity.

19 Example 3

20 A piece of wrought Grade 430 stainless steel foil, 25  $\mu\text{m}$  thick and measuring  
21 approximately 3 cm x 3 cm was patterned with elongated perforations, approximately 150  $\mu\text{m}$   
22 long by 15  $\mu\text{m}$  wide and spaced at about 200  $\mu\text{m}$  micron centres using photo lithography. The  
23 etchant used was ferric chloride. An unperforated piece of wrought Grade 430 stainless steel  
24 foil was coated with a 5  $\mu\text{m}$  thick "loaded" sol-gel coating of yttria stabilized as in Example 1.  
25 A yttria zirconia sol was then sprayed on top of the "filled" sol-gel coating and the perforated  
26 foil was pressed to and held against the wet sol coating. This sandwich structure was then heat  
27 treated to crystalize the sol coating and simultaneously bond the laminated structure. This  
28 example demonstrated the feasibility of using low-temperature sol-gel based processes to build a  
29 complete electrochemical cell structure incorporating a metal foil as a supporting substrate  
30 and/or as part of both of the cell's electrodes.

31 Example 4

32 A piece of wrought Grade 430 stainless steel as in Example 2 and having approximately  
33 5cm x 3 cm in area was prepared by heat treating in air at 550° C for 30 minutes. A "loaded"

1 sol gel coating approximately 5  $\mu\text{m}$  in thickness was applied to one side of the stainless steel foil  
2 as in Example 1. On top of the "loaded" sol-gel coating an approximately 7  $\mu\text{m}$  thick of Grade  
3 320 stainless steel was deposited by DC magnetron sputtering by Thin Film Technology, Inc. of  
4 Buellton, California. This sample was subjected to thermal cycling tests as in Example 1 and  
5 exhibited no delamination after 5 cycles.

6 Example 5

7 A multilayer structure having a first metal layer consisting of a 25  $\mu\text{m}$  thick Grade 430  
8 wrought stainless steel foil was prepared as outlined in Example 2. A porous "loaded" sol gel  
9 coating of yttria stabilized zirconia, approximately 6  $\mu\text{m}$  in thickness, was applied to one side of  
10 the stainless steel foil as in Example 1. To the top of this layer 5 coats of yttria containing  
11 zirconia sol were applied and heat treated to impregnate and seal the top approximately 3  $\mu\text{m}$  of  
12 the "loaded" sol-gel coating. On top of this layer an additional porous "loaded" sol gel coating  
13 approximately 3  $\mu\text{m}$  in thickness was applied as in Example 1. A 0.5  $\mu\text{m}$  layer of gold was  
14 applied by DC sputtering to form a top metal layer. A layer of resist was applied to the gold  
15 surface. The stainless foil was patterned and perforations formed using photolithography and a  
16 ferric chloride etch. The patterned stainless foil was protected by a resist and the gold layer  
17 patterned and was etched with perforations using a standard gold etch (iodine and sodium  
18 iodide). In this way a structure, incorporating perforated metallic layers, suitable for application  
19 as a solid oxide fuel cell was obtained. A piece of this laminated structure measuring  
20 approximately 1.5 cm x 1.5 cm in area exhibited no delamination after thermal cycling as in  
21 Example 1 for 5 cycles.

22 Example 6

23 A multilayer structure having a first metal layer consisting of 25  $\mu\text{m}$  thick Grade 430  
24 wrought stainless steel foil was prepared as outlined in Example 2. A porous "loaded" sol gel  
25 coating approximately 3  $\mu\text{m}$  in thickness was applied to one side of the stainless steel foil as in  
26 Example 1. On top of this layer an additional of 5  $\mu\text{m}$  thick layer of dense yttria stabilized  
27 zirconia was deposited using electron beam evaporation. A 1  $\mu\text{m}$  layer of gold was applied by  
28 DC sputtering at Micralyne Inc. of Edmonton, Alberta, to form a top metal layer. A layer of  
29 resist was applied to the gold surface. The stainless foil was patterned and perforations were  
30 formed using photolithography and a ferric chloride etch. The patterned stainless foil was  
31 protected by a resist and the gold layer was patterned and etched with perforations using a  
32 standard gold etch. In this way a structure suitable for application as a solid oxide fuel cell was  
33 obtained.

## 1 Example 7

2 A multilayer structure having a first metal layer consisting of 25  $\mu\text{m}$  thick Grade 430  
3 stainless steel was prepared as outlined in Example 2. A porous "loaded" sol gel coating  
4 approximately 3  $\mu\text{m}$  in thickness was applied to one side of the stainless steel foil as in Example  
5 1. On top of this layer an additional dense layer of 5  $\mu\text{m}$  of dense yttria stabilized zirconia was  
6 deposited using electron beam evaporation. The stainless foil was patterned and perforations  
7 were formed using photolithography and a ferric chloride etch. A layer of thick film platinum  
8 paste was applied by screen printing to form a top metal layer. In this way a structure suitable  
9 for application as a solid oxide fuel cell was obtained.

## 10 Example 8

11 A multilayer structure having a first metal layer consisting of a 25  $\mu\text{m}$  thick Grade 430  
12 wrought stainless steel foil was prepared as outlined in Example 2. A multi-phase porous  
13 "loaded" sol gel coating approximately 4  $\mu\text{m}$  in thickness was applied to one side of the  
14 stainless steel foil using the technique of Example 1. However, in this example the finished  
15 "loaded" sol-gel coating consisted of nominally 2  $\mu\text{m}$  sized particles of strontium doped  
16 lanthanum chromite and gadolinia doped ceria, in an approximately equal ratio by weight,  
17 encapsulated in a continuous matrix of a yttria stabilized zirconia sol-gel coating. A stabilized  
18 zirconia porous "loaded" sol gel coating approximately 3  $\mu\text{m}$  in thickness was applied as in  
19 Example 1 to the top side of the multi-phase porous "loaded" sol-gel coating. To the top of this  
20 layer multiple coats of yttria containing zirconia sol were applied and heat treated to impregnate  
21 and seal the stabilized zirconia porous "loaded" sol-gel coating. On top of this "sealed"  
22 stabilized zirconia layer a second multi-phase porous "loaded" sol gel coating, similar to the first  
23 one, was applied. This structure indicated the feasibility of using the "loaded" sol-gel process in  
24 combination with sol-gel impregnation to build solid electrolyte electrochemical cells with  
25 porous electrodes incorporating multiple ionic, electronic and mixed conducting electrolyte  
26 phases, as well as a non-porous central electrolyte membrane.

27 All publications mentioned in this specification are indicative of the level of skill of  
28 those skilled in the art to which this invention pertains. All publications are herein incorporated  
29 by reference to the same extent as if each individual publication was specifically and  
30 individually indicated to be incorporated by reference.

31 The terms and expressions in this specification are, unless otherwise specifically defined  
32 herein, used as terms of description and not of limitation. There is no intention, in using such  
33 terms and expressions, of excluding equivalents of the features illustrated and described.

1 We claim:

2 1. A flexible, metal-supported, solid electrolyte electrochemical cell comprising:

3 a) a central, non-porous, ionically- or mixed ionically- and electronically-conducting  
4 electrolyte membrane which is less than 10 µm thick and defines two major surfaces,  
5 one major surface on each side of the central electrolyte membrane;

6 b) a first, non-porous, metallic layer which is adhered to one of the major surfaces of the  
7 central electrolyte membrane, and having a plurality of perforations extending  
8 therethrough forming a first pattern of perforations;

9 c) a second, non-porous, metallic layer which is adhered to the other of the major surfaces  
10 of the central electrolyte membrane, and having a plurality of perforations extending  
11 therethrough forming a second pattern of perforations;

12 d) a first outer, non-porous, ionically- or mixed ionically- and electronically-conducting  
13 electrolyte layer which is:

14 - adhered to the first metallic layer and makes intimate contact with the central  
15 electrolyte membrane through the first pattern of perforations, and

16 - continuously ionically-conductive throughout its bulk, and electronically-conductive  
17 through its thickness from the underlying first metallic layer to any reacting gases at  
18 its outer surface;

19 e) a first, ionically-conductive, interface formed at a contact surface between the first outer  
20 electrolyte layer and the central electrolyte membrane;

21 f) a first, electronically-conductive, interface formed at a contact surface between the first  
22 metallic layer and the first outer electrolyte layer;

23 g) a second outer, non-porous, ionically- or mixed ionically- and electronically-conducting  
24 electrolyte layer which is:

25 - adhered to the outer surface of the second metallic layer and makes intimate contact  
26 with the central electrolyte membrane through the second pattern of perforations, and

27 - continuously ionically-conductive throughout its bulk, and electronically-conductive  
28 through its thickness from the underlying second metallic layer to any reacting gases  
29 at its outer surface;

30 h) a second, ionically-conductive interface formed at a contact surface between the second  
31 outer electrolyte layer and the central electrolyte membrane; and

1        i) a second, electronically-conductive <sup>40</sup> interface formed at a contact surface between the  
2        second metallic layer and the second outer electrolyte layer.

3        2. The electrochemical cell of claim 1, wherein the first and second pattern of perforations  
4        are arranged such that the perforations are not aligned on either side of the central  
5        electrolyte membrane.

6        3. The electrochemical cell of claim 1, wherein the first and second pattern of perforations  
7        are arranged such that in areas, the perforations are aligned on either side of the central  
8        electrolyte, leaving the central electrolyte exposed in those aligned areas.

9        4. The electrochemical cell of claims 1, 2 or 3, wherein one or both of the first and second  
10      pattern of perforations are arranged so as to vary electrochemical current density, by  
11      varying the density of the perforations from one area to another over the surface of the  
12      first and second metallic layer.

13      5. The electrochemical cell of claim 1, which further comprises first and second metallic  
14      interconnect elements connected with gas tight seals to the first and second metallic  
15      layers respectively for providing electrical contact from the electrochemical cell to  
16      another electrochemical cell, to form gas tight gas supply channels to provide gas to the  
17      first and second outer electrolyte layers, and to form gas tight gas exhaust channels for  
18      removing exhaust gases from the first and second outer electrolyte layers.

19      6. The electrochemical cell of claim 5, wherein the gas tight seals and the electrical contact  
20      between the first and second metallic interconnect elements and the first and second  
21      metallic layers respectively are provided by metallurgical bonds.

22      7. The electrochemical cell of claim 6, wherein the first and second metallic interconnect  
23      elements are formed with any combination of raised or depressed ridges or dimples  
24      across their surfaces, and a thickened section formed around its perimeter to provide  
25      openings for the gas supply and exhaust channels.

26      8. The electrochemical cell of claim 7, wherein the metallurgical bonds are formed by one  
27      or both of vacuum brazing and inert atmosphere brazing.

28      9. The electrochemical cell of claim 1, wherein:  
29        - the first and second metallic layers are formed from one or more of nickel, gold,  
30        silver, platinum, chromium, chromium-iron alloys, ferritic stainless steels, austenitic  
31        stainless steels, and nickel based super alloys; and

1        - one or more of the central electrolyte membrane, and the first and second outer  
2        electrolyte layers are ionically- or mixed ionically- and electronically-conducting and  
3        are formed from one or more of fully stabilized zirconia, partially stabilized zirconia,  
4        doped ceria, doped bismuth oxide and perovskite oxides; and  
5        - one or more of the central electrolyte membrane, and the first and second outer  
6        electrolyte layers are mixed ionically and electronically-conducting and are formed  
7        from one or more of perovskite oxides, platinum, palladium and silver, and oxides  
8        of silver.

9        10. The electrochemical cell of claim 1, wherein:

10        - the first and second metallic layers are formed from one or more of ferritic stainless  
11        steels and nickel based super alloys; and  
12        - one or more of the central electrolyte membrane, and the first and second outer  
13        electrolyte layers are ionically- or mixed ionically- and electronically-conducting and  
14        are formed from one or more of fully stabilized zirconia, partially stabilized zirconia,  
15        and doped ceria; and  
16        - one or more of the central electrolyte membrane, and the first and second outer  
17        electrolyte layers are mixed ionically and electronically-conducting and are formed  
18        from one or more of perovskite oxides.

19        11. The electrochemical cell of claim 1, 7 or 8, wherein one or both of the first and second  
20        metallic layers are formed from wrought metal or alloy foils.

21        12. A flexible, metal-supported, solid electrolyte electrochemical cell comprising:

22        a) a central, non-porous, ionically- or mixed ionically- and electronically-conducting  
23        electrolyte membrane which is less than 10  $\mu\text{m}$  thick and defines two major surfaces,  
24        one major surface on each side of the electrolyte membrane;  
25        b) a first, porous, inner electrolyte layer which is less than 10  $\mu\text{m}$  thick, is ionically- or  
26        mixed ionically- and electronically-conducting, and is adhered to one of the major  
27        surfaces of the central electrolyte membrane;  
28        c) a first, non-porous, metallic layer which is adhered to the outer surface of the first inner  
29        electrolyte layer, and having a plurality of perforations extending therethrough forming a  
30        first pattern of perforations;

- 1       d) a first, inner, ionically-conductive interface formed at a contact surface between the  
2                    central electrolyte membrane and the first inner electrolyte layer;
- 3       e) a first, inner, electronically-conductive interface formed at a contact surface between the  
4                    first inner electrolyte layer and the first metallic layer;
- 5       f) a second, porous, inner electrolyte layer which is less than 10 µm thick, is ionically- or  
6                    mixed ionically and electronically-conducting, and is adhered to the other of the major  
7                    surfaces of the central electrolyte membrane;
- 8       g) a second, non-porous, metallic layer which is adhered to the outer surface of the second  
9                    inner electrolyte layer, and having a plurality of perforations extending therethrough  
10                  forming a second pattern of perforations;
- 11      h) a second, inner, ionically-conductive interface formed at a contact surface between the  
12                    central electrolyte membrane and the second inner electrolyte layer;
- 13      i) a second, inner, electronically-conductive interface formed at a contact surface between  
14                    the second inner electrolyte layer and the second metallic layer.

15     13. The electrochemical cell of claim 12 wherein, the first and second pattern of perforations  
16                  are arranged such that perforations are not aligned on either side of central electrolyte  
17                  layer.

18     14. The electrochemical cell of claim 12 or 13, wherein one or both of the first and second  
19                  pattern of perforations are arranged so as to vary the electrochemical current density, by  
20                  varying the density of perforations from one area to another over the surface of the first  
21                  and second metallic layers.

22     15. The electrochemical cell of claim 12, which further comprises: first and second metallic  
23                  interconnect elements connected with gas tight seals to the first and second metallic  
24                  layers respectively for providing electrical contact from the electrochemical cell to  
25                  another electrochemical cell, to form gas tight gas supply channels to provide gas to the  
26                  outer surfaces of the first and second metallic layers, and to form gas tight gas exhaust  
27                  channels for removing exhaust gases from the first and second metallic layers.

28     16. The electrochemical cell of claim 15, wherein the gas tight seals and the electrical  
29                  contact between the first and second metallic interconnect elements and the first and  
30                  second metallic layers respectively are provided by metallurgical bonds.

31     17. The electrochemical cell of claim 16, wherein the first and second metallic interconnect  
32                  elements are formed with any combination of raised or depressed ridges or dimples

1 across their surfaces, and a thickened section formed around its perimeter to provide  
2 openings for the gas supply and exhaust channels.

3 18. The electrochemical cell of claim 17, wherein the metallurgical bonds are formed by one  
4 or both of vacuum brazing and inert atmosphere brazing.

5 19. The electrochemical cell of claims 12, wherein one or both of the first inner  
6 electronically-conductive interface and the second inner electronically-conductive  
7 interface are modified, by a metal coating on the inner surface of one or both of the first  
8 and second metallic layers, the metal coating being capable of being converted to metal  
9 oxide compositions that enhance one or both of the electronic conductivity and the  
10 stability of the interfaces.

11 20. The electrochemical cell of claim 12, wherein:

12 - the first and second metallic layers are formed from one or more of nickel, gold,  
13 silver, platinum, chromium, chromium-iron alloys, ferritic stainless steels, austenitic  
14 stainless steels, and nickel based super alloys; and

15 - one or more of the central electrolyte membrane, and the first and second inner  
16 electrolyte layers are ionically- or mixed ionically- and electronically-conducting and  
17 are formed from one or more of fully stabilized zirconia, partially stabilized zirconia,  
18 doped ceria, doped bismuth oxide, perovskite oxides and pyrochlore oxides; and

19 - one or more of the central electrolyte membrane and the first and second inner  
20 electrolyte layers are mixed ionically- and electronically-conducting and are formed  
21 from one or more of perovskite oxides, platinum, palladium and silver, and oxides  
22 of silver.

23 21. The electrochemical cell of claim 12, wherein:

- the first and second metallic layers are formed from one or more of ferritic stainless steels, and nickel based super alloys; and
- one or more of the central electrolyte membrane, and the first and second inner electrolyte layers are ionically- or mixed ionically- and electronically-conducting and are formed from one or more of fully stabilized zirconia, partially stabilized zirconia, and doped ceria; and
- one or more of the central electrolyte membrane and the first and second inner electrolyte layers are mixed ionically- and electronically-conducting and are formed from of perovskite oxides.

- 1 22. The electrochemical cell of claim 12, 20 or 21, wherein one or both of the first and  
2 second metallic layers are formed from metal or metal alloy foils.
- 3 23. The electrochemical cell of claim 12, wherein one or both of the first and second inner  
4 electrolyte layer is in the form of a coating comprising particles of ionically-conducting,  
5 mixed ionically- and electronically-conducting, or electronically-conducting materials,  
6 encapsulated in, and bonded together by, a sol-gel of an ionically-conducting or mixed  
7 ionically- and electronically- conducting ceramic oxide material.
- 8 24. The electrochemical cell of claim 23, wherein the central electrolyte membrane is in the  
9 form of a coating comprising particles of ionically-conducting, mixed ionically- and  
10 electronically-conducting, or electronically-conducting materials, encapsulated in, and  
11 bonded together by, a sol-gel of an ionically-conducting or mixed ionically- and  
12 electronically-conducting ceramic oxide material, and further impregnated with one or  
13 more sol-gels to seal off interconnected porosity.
- 14 25. The electrochemical cell of claim 12, which further comprises one or both of:
  - 15 - a first, outer, electrolyte layer formed of one or more metal oxide ceramics, and  
16 adhered to the outer surface of the first metallic layer; and
  - 17 - a second, outer, electrolyte layer formed of one or more metal oxide ceramics,  
18 and adhered to the outer surface of the second metallic layer.
- 19 26. The electrochemical cell of claim 25, wherein one or both of the first and second outer  
20 electrolyte layers include hydrocarbon fuel reforming or selective oxidation catalysts,  
21 selected from metals and oxides of metals from Groups II, V, VI, VII, VIII, IX, X, XI,  
22 XV and the F Block lanthanides of the Periodic Table of elements.
- 23 27. The electrochemical cell of claim 23 or 24, for use as a solid oxide fuel cell, wherein:
  - 24 - the first metallic layer is formed from a wrought ferritic stainless steel foil;
  - 25 - the central electrolyte membrane is formed of stabilized zirconia;
  - 26 - the second metallic layer is formed as a coating from ferritic stainless steel;
  - 27 - the first and second inner electrolyte layers are mixed ionically- and electronically-  
28 conducting and are formed of one or more of stabilized zirconia, doped ceria and  
29 lanthanum strontium chromite.
- 30 28. The electrochemical cell of claim 23 or 24, for use as a solid oxide fuel cell, wherein:

45

- 1 - the first metallic layer and the second metallic layer are formed from a wrought
- 2 ferritic stainless steel foil;
- 3 - the central electrolyte membrane is formed of stabilized zirconia;
- 4 - the first and second inner electrolyte layers are mixed ionically- and electronically-
- 5 conducting and are formed of one or more of stabilized zirconia, doped ceria and
- 6 lanthanum strontium chromite.

7 29. A metallurgically bonded, multi-cell, solid electrolyte electrochemical reactor assembly

8 formed from a plurality of metal-supported solid electrolyte electrochemical cells, each

9 of which has an anode and cathode electrode, and which are connected in electrical

10 series, comprising:

11 a) a plurality of flexible, metal-supported, solid electrolyte electrochemical cells as

12 defined in one of claims 1, 12, 22, 23, or 27, wherein each of the first metallic layer

13 and the second metallic layer function individually as a component of, and an

14 electronic current collector or distributor for, either the anode or cathode electrode of

15 the cell, such that if the first metallic layer forms part of the cell's anode electrode

16 then the second metallic layer forms part of the cell's cathode electrode and vice

17 versa;

18 b) metallic interconnect elements between which the electrochemical cells are

19 interleaved, each such metallic interconnect element being formed with any

20 combination of raised or depressed ridges or dimples across its surface, and a

21 thickened section formed around its perimeter with channels formed therein around

22 its perimeter, such that when metallurgically bonded to the first or second metallic

23 layer of the adjoining electrochemical cells gas-tight seals and electrical contacts are

24 formed between the first or second metallic layer of the adjoining cells and the

25 metallic interconnect element, providing gas flow channels across the outer surfaces

26 of the adjoining cells as well as electrical interconnection between the adjoining

27 cells;

28 c) openings located around the perimeter of the electrochemical cells and aligned with

29 matching openings in the metallic interconnect elements, such that when the cells

30 and the interconnect elements are metallurgically bonded together, these openings

31 align to provide gas supply and exhaust manifolds, running transversely to the plane

32 of the cells and the metallic interconnect elements, for gas flow communication with

33 any gas flow channels at the outer surfaces of the cells;

- 1 d) a top end assembly which is metallurgically bonded to the topmost metallic
- 2 interconnect element and which provides gas flow communication between the gas
- 3 supply and exhaust manifolds and any gas supply and exhaust piping that is external
- 4 to the reactor assembly;
- 5 e) a bottom end assembly which is metallurgically bonded to the bottommost metallic
- 6 interconnect element and which seals off the ends of the gas supply and exhaust
- 7 manifolds and directs gas flows to and from the bottommost electrochemical cell;
- 8 f) the reactor assembly and any of its structural supports being electrically isolated, and
- 9 the reactor assembly and any external gas supply and exhaust piping being
- 10 electrically isolated; and
- 11 g) two external electrical terminations, one connected to the top end assembly and the
- 12 other connected to the bottom end assembly.

13 30. The reactor assembly of claim 29, wherein a plan projection of the cells and the metallic  
14 interconnect elements is rectangular in shape, and wherein the gas supply and exhaust  
15 manifolds are arranged along both of the long sides of the rectangle.

16 31. The reactor assembly of claim 30, wherein the metallurgical bonds are formed one or  
17 both of vacuum brazing and inert atmosphere brazing.

18 32. The reactor assembly of claim 31, wherein the metal-supported electrochemical cells are  
19 as set forth in claim 1.

20 33. The reactor assembly of claim 31, wherein the metal-supported electrochemical cells are  
21 as set forth in claim 12.

22 34. The reactor assembly of claim 31, wherein the metal-supported electrochemical cells are  
23 as set forth in claim 22..

24 35. The reactor assembly of claim 31, wherein the metal-supported electrochemical cells are  
25 as set forth in claim 23.

26 36. The reactor assembly of claim 31, wherein the metal-supported electrochemical cells are  
27 as set forth in claim 27.

28 37. A process of forming a flexible metal-supported solid electrolyte electrochemical cell,  
29 comprising:

- 30 a) providing a wrought metal or alloy foil to form a first metallic layer and to function as a
- 31 supporting substrate;

47

- 1 b) applying a non-porous, ionically-conducting or mixed ionically- and electronically-  
2 conducting electrolyte coating, which is less than 10  $\mu\text{m}$  thick, to one surface of the first  
3 metallic layer to form a central electrolyte membrane;
- 4 c) applying a non-porous metallic coating on top of the central electrolyte membrane to  
5 form a second metallic layer;
- 6 d) forming a first pattern of perforations in the first metallic layer;
- 7 e) forming a second pattern of perforations in the second metallic layer;
- 8 f) applying a first, non-porous, mixed ionically- and electronically-conducting electrolyte  
9 coating, which is less than 4  $\mu\text{m}$  thick, over the outer surface of the first metallic layer to  
10 provide a first outer electrolyte layer; and
- 11 g) applying a second, non-porous, mixed ionically- and electronically-conducting  
12 electrolyte coating, which is less than 4  $\mu\text{m}$  thick, over the outer surface of the second  
13 metallic layer to provide a second outer electrolyte layer.

14 38. The process of claim 37, wherein the perforations in each of the first and second metallic  
15 layers are formed by etching with a photo-chemical machining process.

16 39. The process of claim 37 or 38, wherein:

- 17 - the second metallic layer is formed by one or more of DC sputtering, e-beam  
18 evaporation, and electro-plating; and
- 19 - the central electrolyte membrane and the first and second outer electrolyte layers are  
20 provided by one or more of reactive DC sputtering, AC sputtering, e-beam evaporation,  
21 polarized electrochemical deposition, multi-layer sol-gel coating, and particle-filled sol-  
22 gel coatings further impregnated with sol-gel coatings.

23 40. A process of forming a flexible metal-supported solid electrolyte electrochemical cell,  
24 comprising:

- 25 a) providing a wrought metal or alloy foil to form a first metallic layer and to function as a  
26 supporting substrate;
- 27 b) applying a porous, ionically- or mixed ionically- and electronically-conducting  
28 electrolyte coating, which is less than 10  $\mu\text{m}$  thick, to one surface of the first metallic  
29 layer to form a first, porous, inner electrolyte layer;

- 1 c) applying a non-porous, ionically-conducting or mixed ionically- and electronically-  
2 conducting electrolyte coating, which is less than 10  $\mu\text{m}$  thick, to the surface of the first  
3 inner electrolyte layer to form a central electrolyte membrane;
- 4 d) applying a porous, ionically-conducting or mixed ionically- and electronically-  
5 conducting electrolyte coating, which is less than 10  $\mu\text{m}$  thick, to the surface of the  
6 central electrolyte membrane to form a second, porous, inner electrolyte layer;
- 7 e) applying a non-porous, metallic coating on top of the second inner electrolyte layer to  
8 form a second metallic layer;
- 9 f) forming a first pattern of perforations in the first metallic layer; and
- 10 g) forming a second pattern of perforations in the second metallic layer.

11 41. The process of claim 40, wherein the perforations in each of the first and second metallic  
12 layers are formed by etching with a photo-chemical machining process.

13 42. The process of claim 40, which further comprises one or both of the steps of:

- 14 a) applying a ceramic electrolyte coating, which is less than 4  $\mu\text{m}$  thick, to the outer surface  
15 of the first metallic layer to provide a first, outer, electrolyte layer; and
- 16 b) applying a ceramic electrolyte coating, which is less than 4  $\mu\text{m}$  thick, to the outer surface  
17 of the second metallic layer to provide a second, outer, electrolyte layer.

18 43. The process of claim 40 wherein:

- 19 - the second metallic layer is formed by one or more of DC sputtering, e-beam  
20 evaporation, and electro plating;
- 21 - the first and second inner electrolyte layers are provided by applying a single layer or  
22 multi layer composite coating, comprising particles of ionically-conducting, mixed  
23 ionically- and electronically-conducting, or electronically-conducting materials,  
24 encapsulated in, and bonded together by, a sol-gel of an ionically-conducting or mixed  
25 ionically- and electronically- conducting ceramic oxide material; and
- 26 - the central electrolyte membrane is provided by one or more of reactive DC sputtering,  
27 AC sputtering, e-beam evaporation, polarized electrochemical deposition, multi-layer  
28 sol-gel coating, and particle-filled sol-gel coatings further impregnated with sol-gel.

29 44. A process of forming a flexible metal-supported solid electrolyte electrochemical cell,  
30 comprising:

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- 1 a) providing a first wrought metal or alloy foil to form a first metallic layer and to function  
2 as a supporting substrate;
- 3 b) providing a second wrought metal or alloy foil substrate to form a second metallic layer;
- 4 c) forming a second pattern of perforations in the second metallic layer;
- 5 d) applying a single layer or multi layer composite porous electrolyte coating, which is less  
6 than 10 µm thick, and which comprises particles of ionically-conducting, mixed  
7 ionically- and electronically-conducting, or electronically-conducting materials,  
8 encapsulated in, and bonded together by, a sol-gel of an ionically-conducting or mixed  
9 ionically- and electronically- conducting ceramic oxide, to one surface of the first  
10 metallic layer to form a first, porous, inner electrolyte layer;
- 11 e) applying a non-porous, ionically-conducting or mixed ionically- and electronically-  
12 conducting electrolyte coating, which is less than 10 µm thick, to the surface of the first  
13 inner electrolyte layer to form a central electrolyte membrane;
- 14 f) applying a porous electrolyte coating, which is less than 10 µm thick, and which  
15 comprises particles of ionically-conducting, mixed ionically- and electronically-  
16 conducting, or electronically-conducting materials, encapsulated in, and bonded together  
17 by, a sol-gel of an ionically-conducting or mixed ionically- and electronically-  
18 conducting ceramic oxide material, to the surface of the central electrolyte membrane  
19 and to one surface of the second metallic layer, bonding the porous electrolyte coating  
20 together to simultaneously form a second, porous, inner electrolyte layer and laminate  
21 the second metallic layer thereto;
- 22 g) forming a first pattern of perforations in the first metallic layer.

23 45. The process of claim 44 wherein the perforations in each of the first and second metallic  
24 layers are formed by etching with a photo-chemical machining process, and wherein  
25 when the first pattern of perforations are formed, the second metallic layer is protected  
26 from the etchant.

27 46. The process of claim 44, which further comprises one or both of the steps of:

- 28 a) applying a ceramic electrolyte coating, which is less than 4 µm thick, to the outer surface  
29 of the first metallic layer to provide a first, outer, electrolyte layer; and
- 30 b) applying a ceramic electrolyte coating, which is less than 4 µm thick, to the outer surface  
31 of the second metallic layer to provide a second, outer electrolyte layer.

1 47. The process of claim 44, wherein the central electrolyte membrane is provided by one or  
2 more of reactive DC sputtering, AC sputtering, e-beam evaporation, polarized  
3 electrochemical deposition, multi-layer sol-gel coating, and particle-filled sol-gel  
4 coatings further impregnated with sol-gel coatings.

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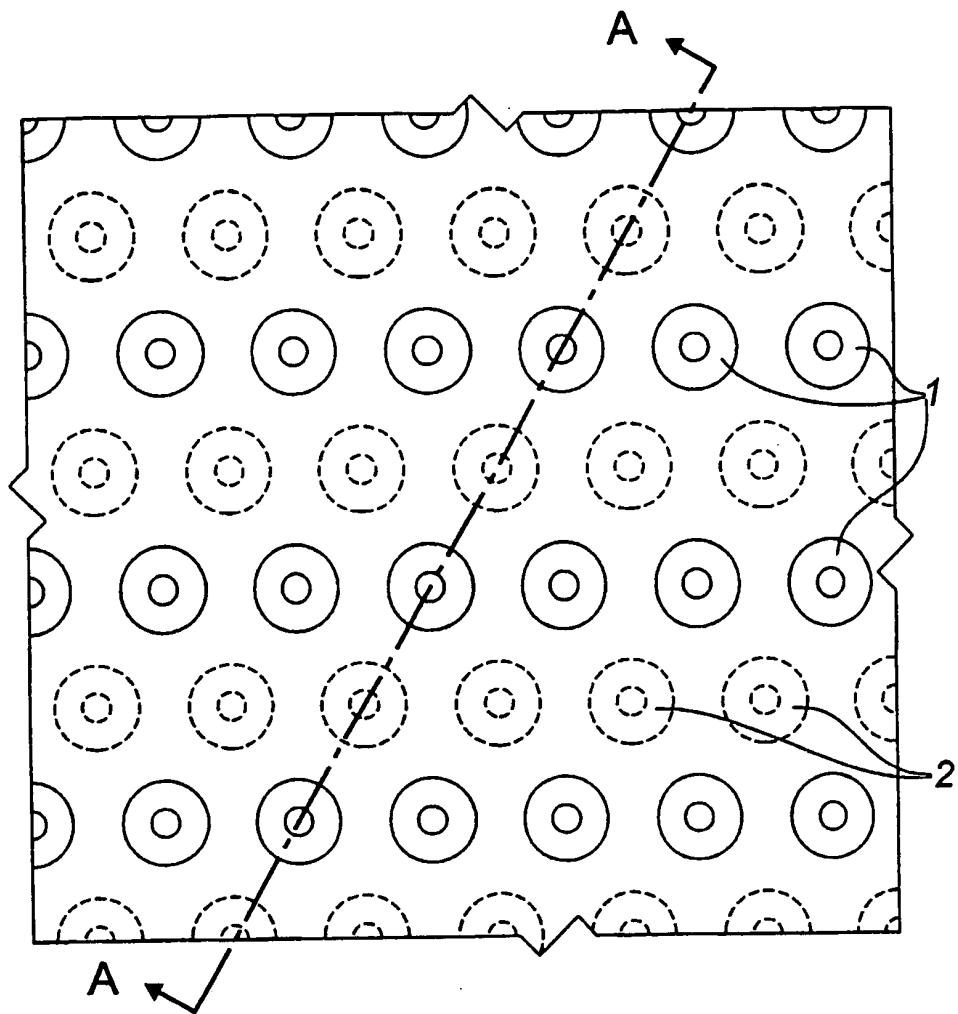


FIG. 1a

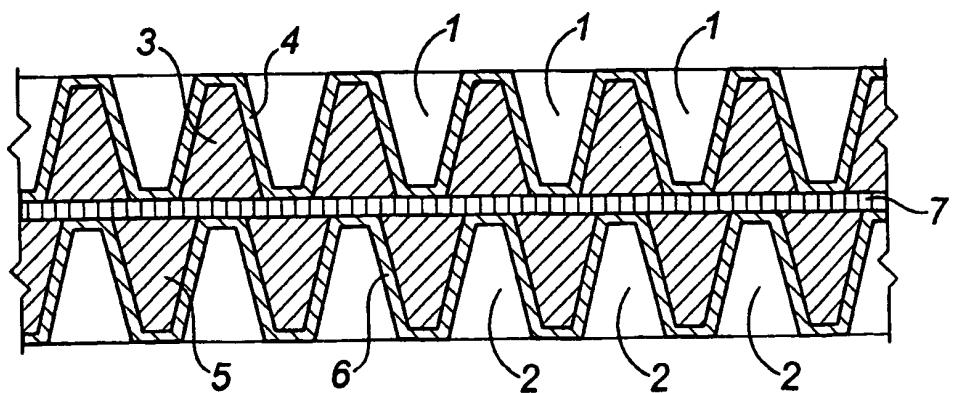


FIG. 1b

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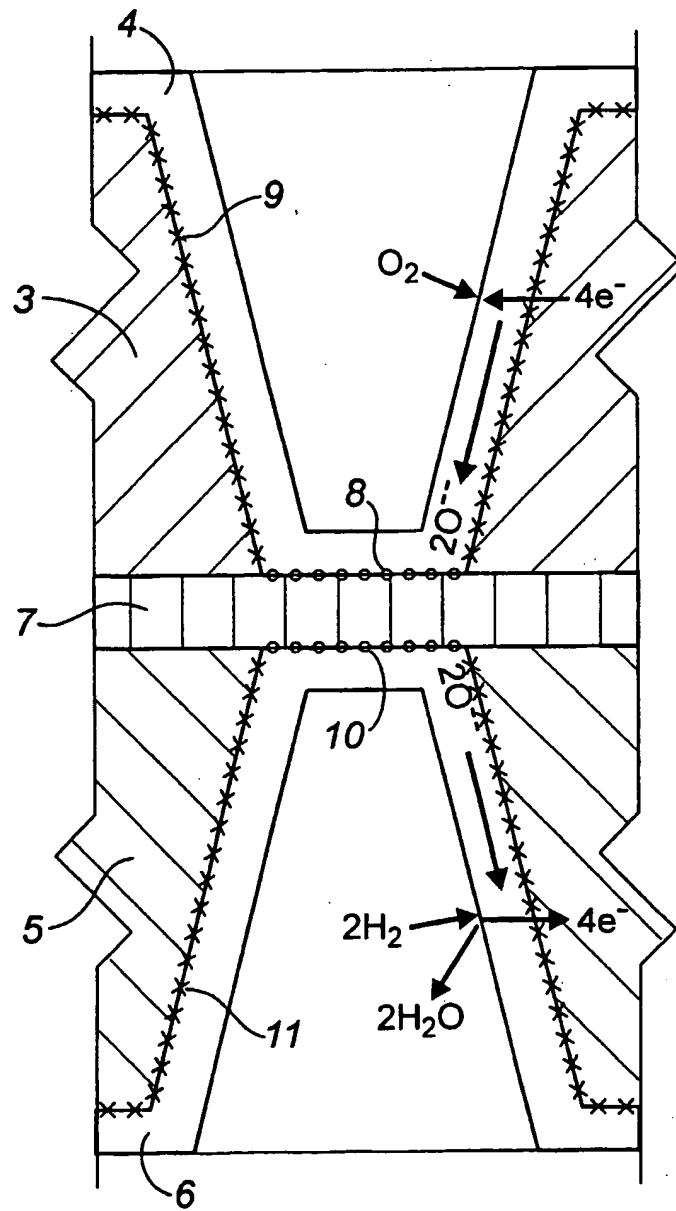


FIG. 2

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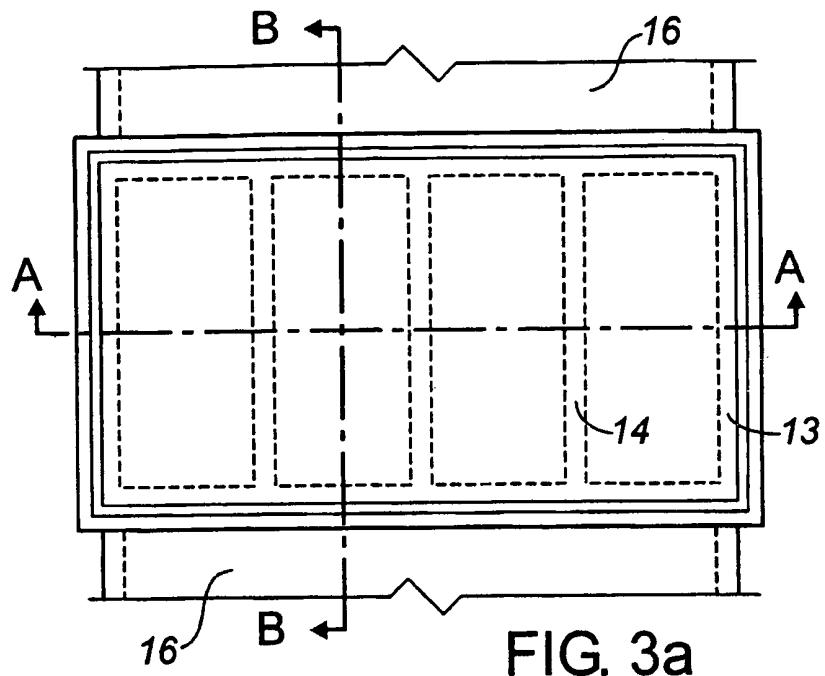


FIG. 3a

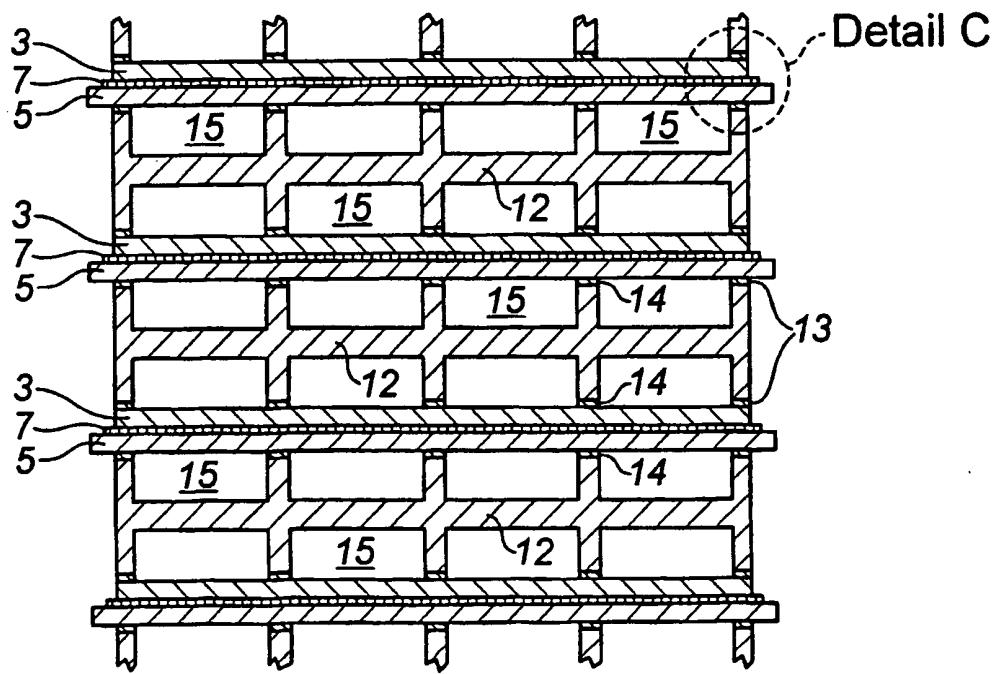


FIG. 3b

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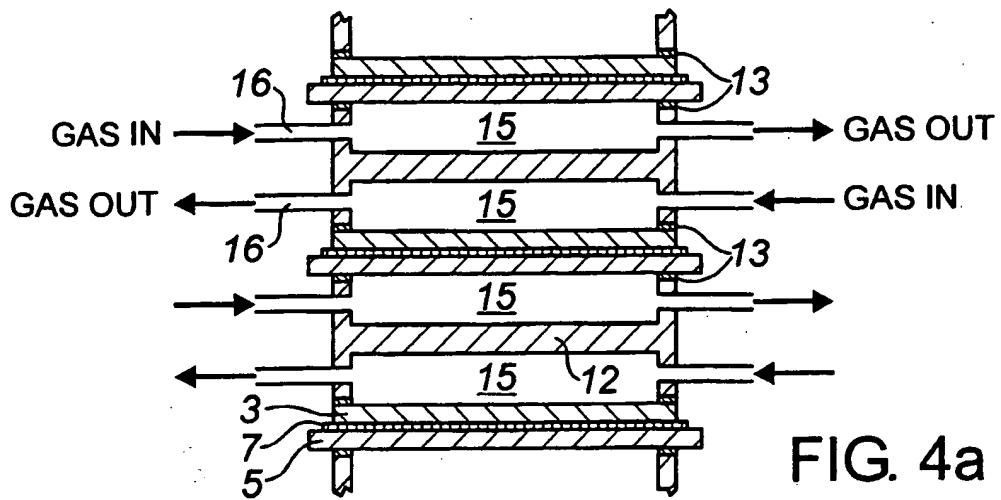
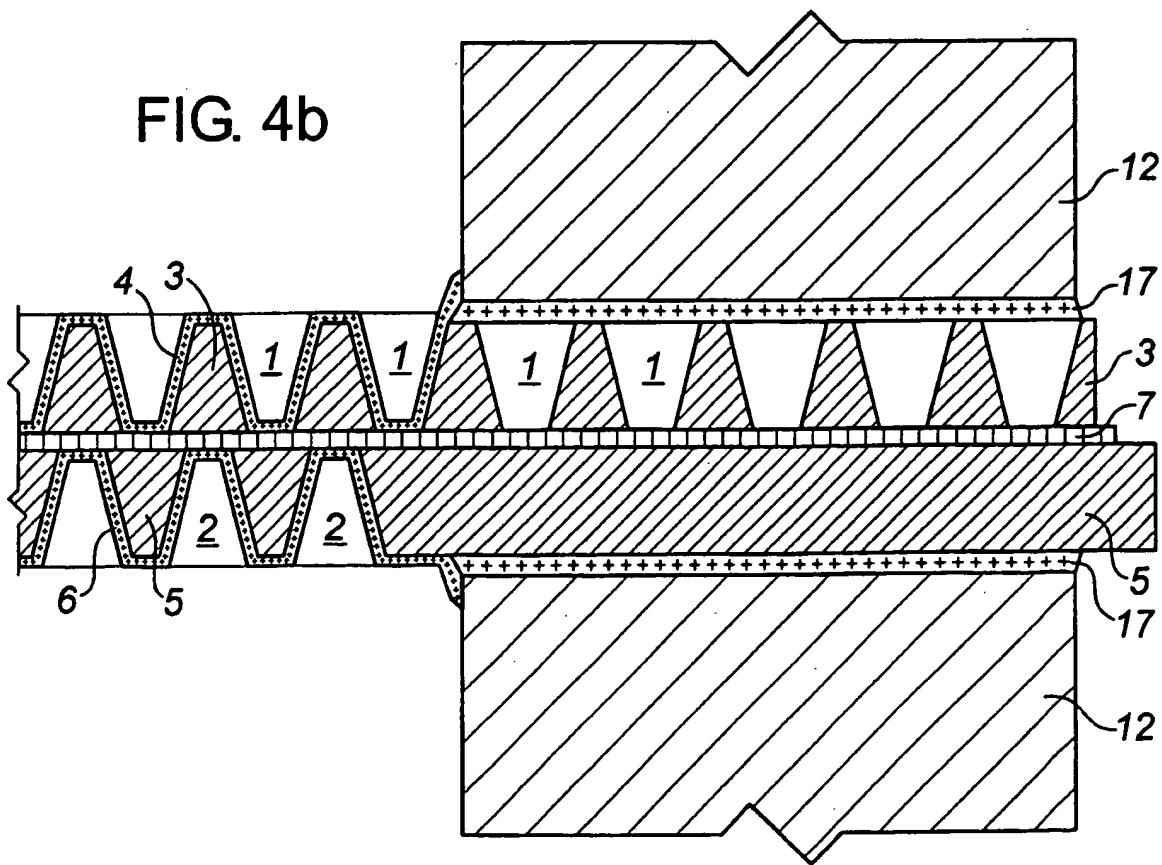


FIG. 4a



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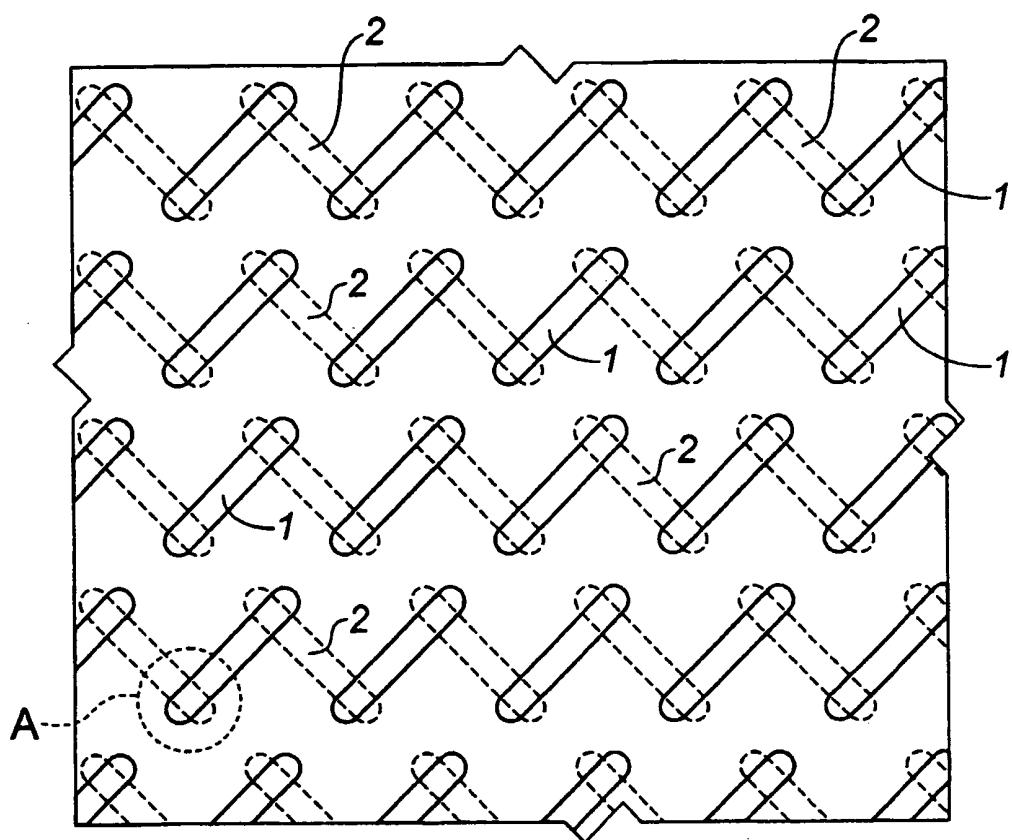


FIG. 5a

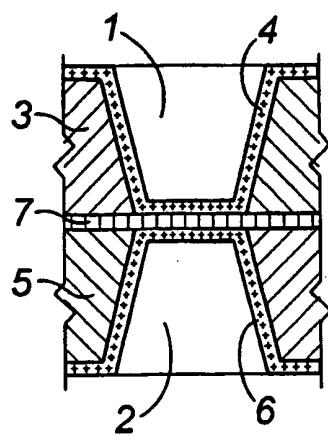


FIG. 5b

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FIG. 6a

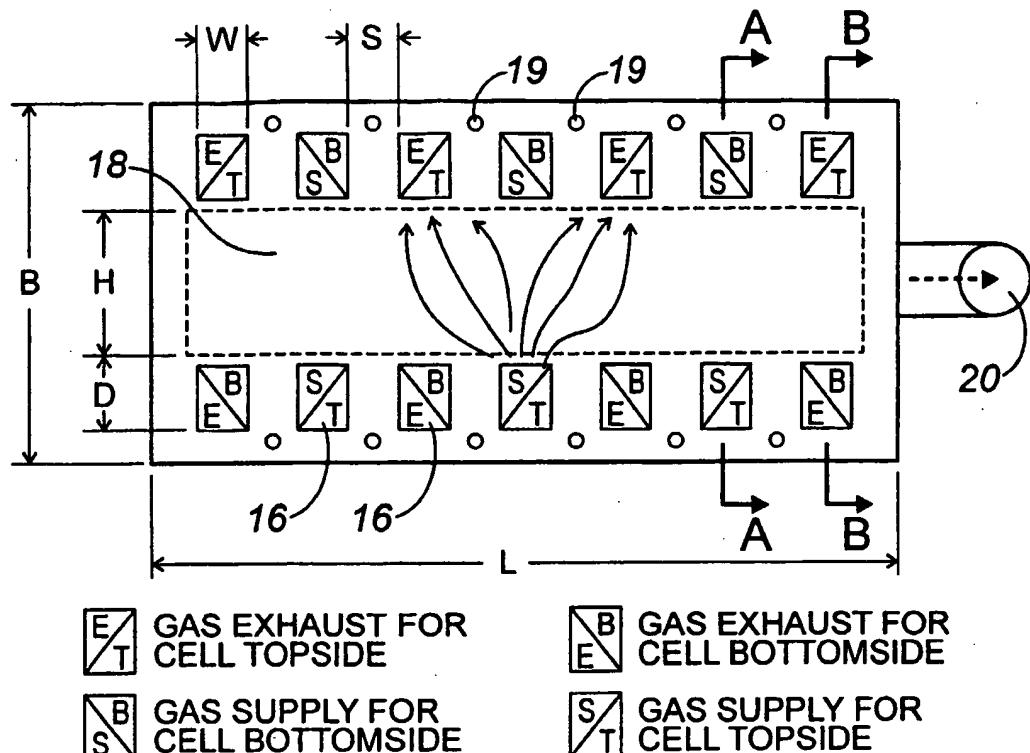


FIG. 6b

FIG. 6c

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FIG. 7a

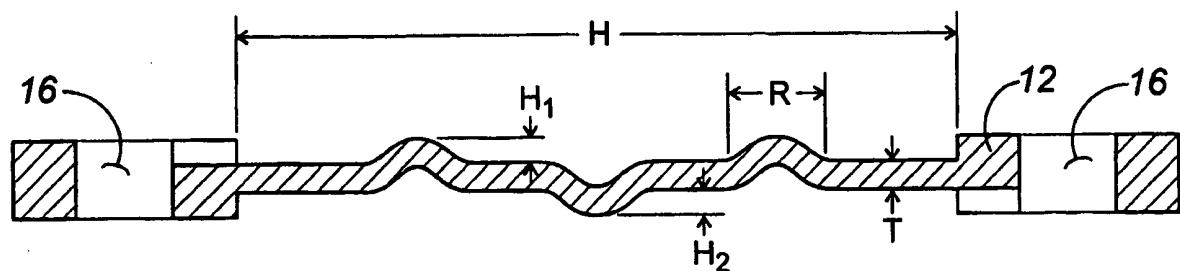
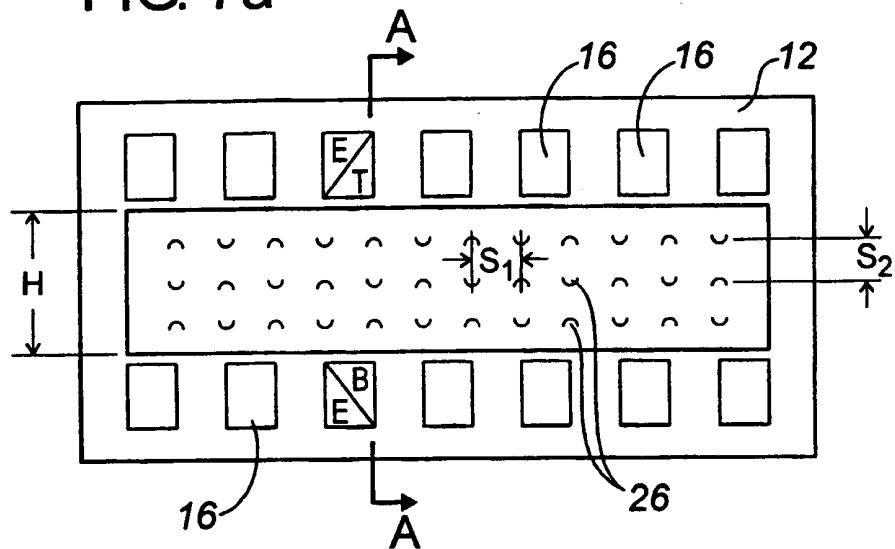
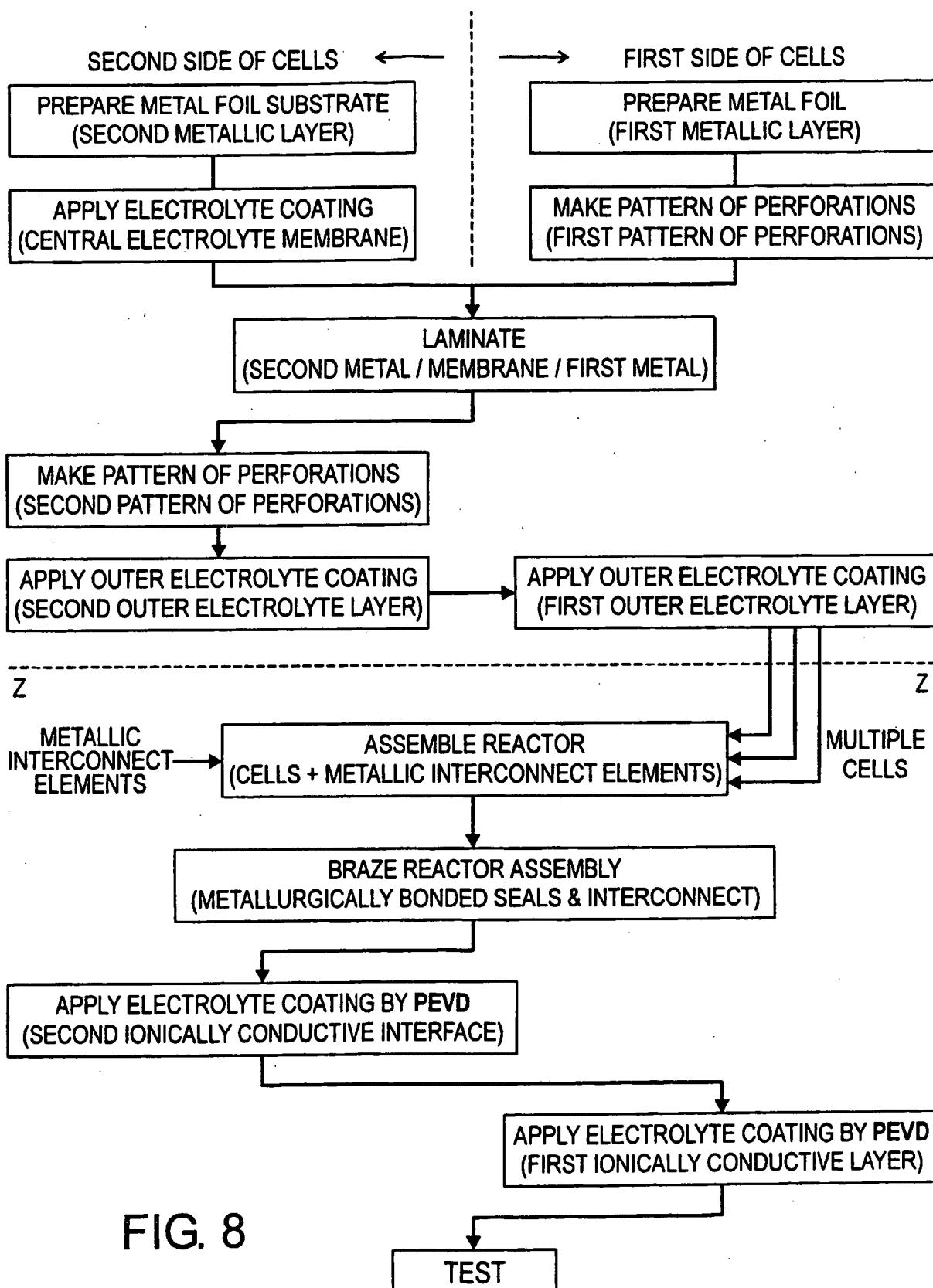


FIG. 7b

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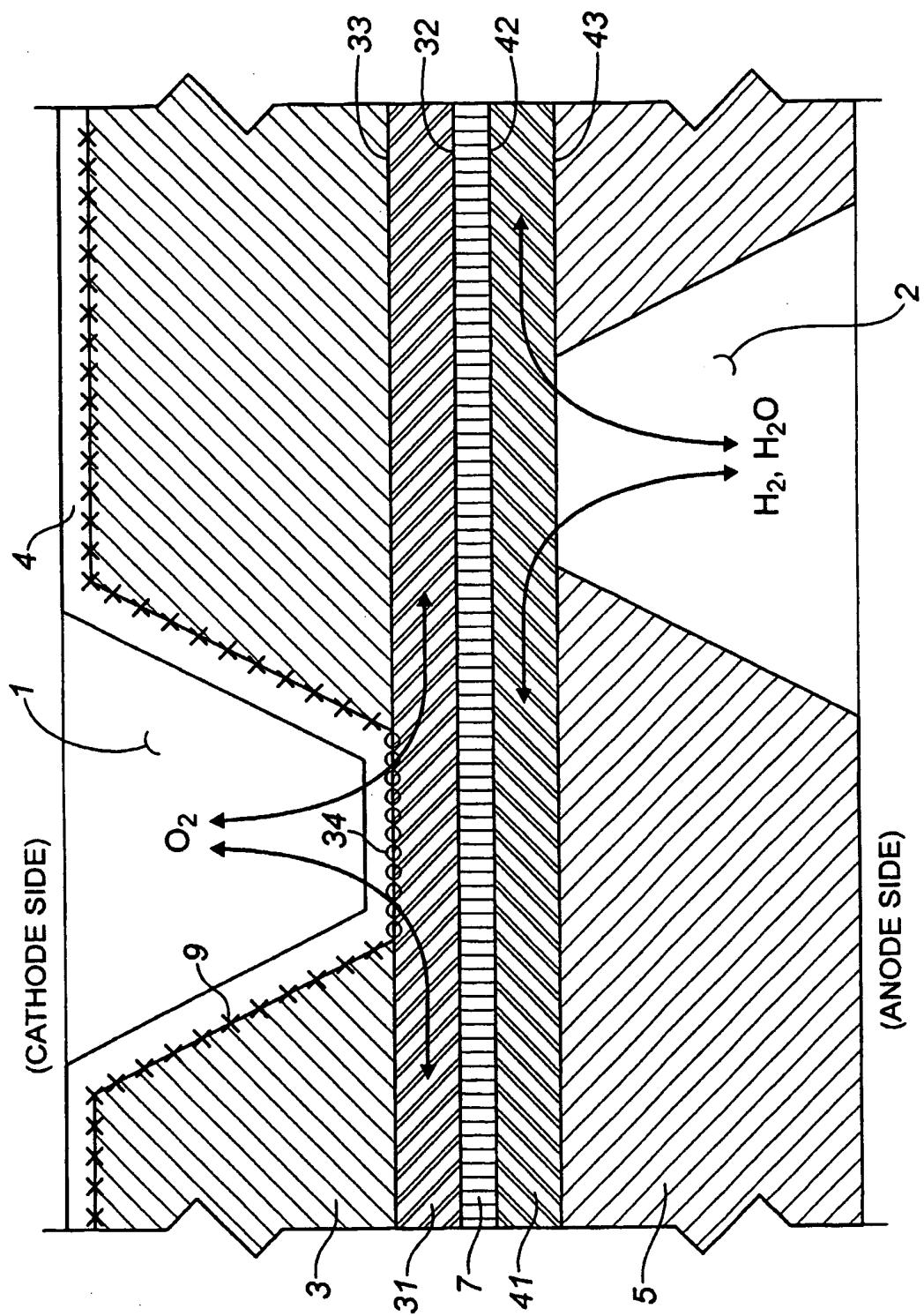


FIG. 9

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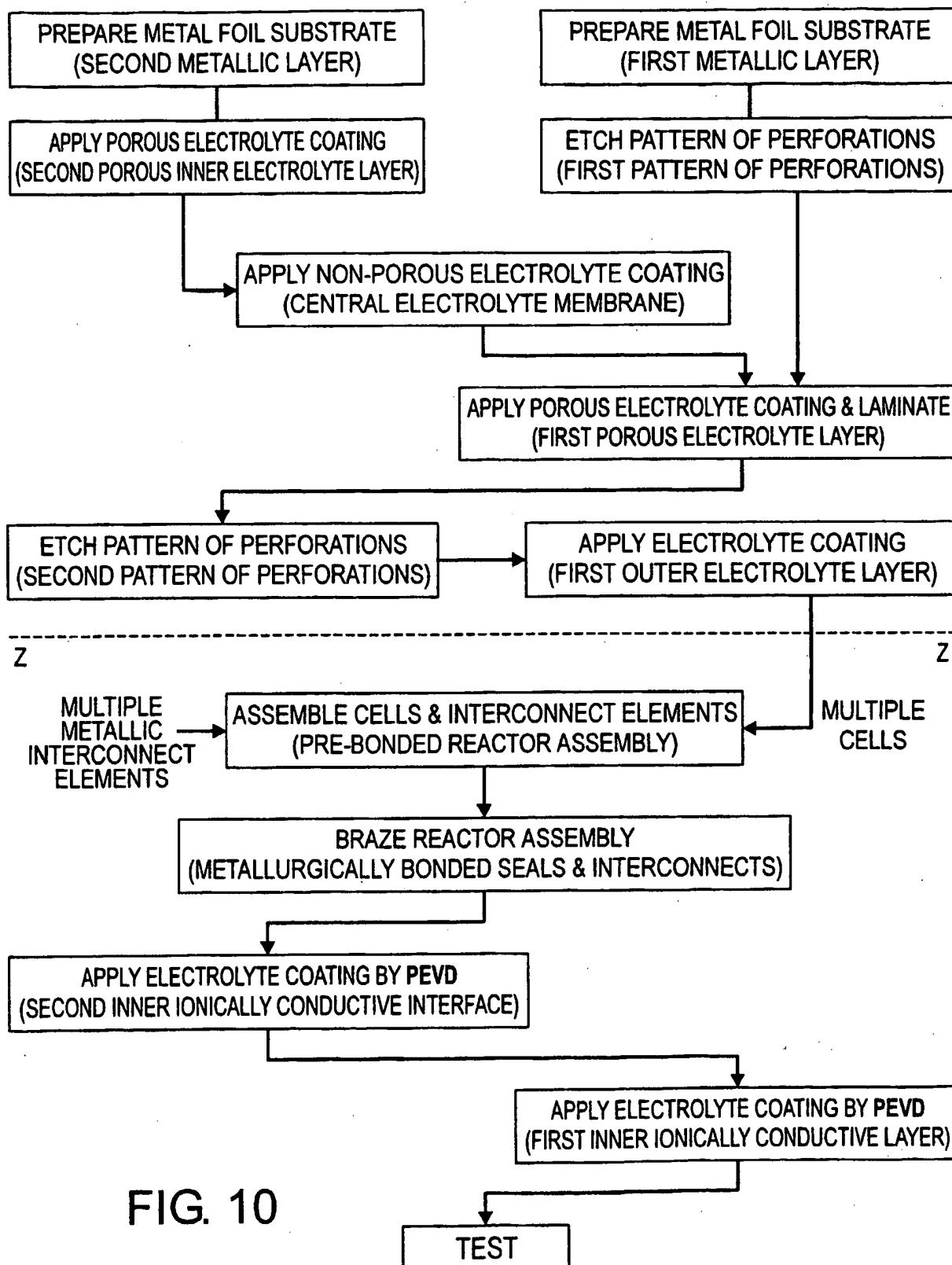


FIG. 10

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(74) Agent: McKAY-CAREY Mary, Jane; McKay-Carey &amp; Company, 2590 Commerce Place, 10155-102 Street, Edmonton, Alberta T5J 4G8 (CA).

(21) International Application Number: PCT/CA02/00582

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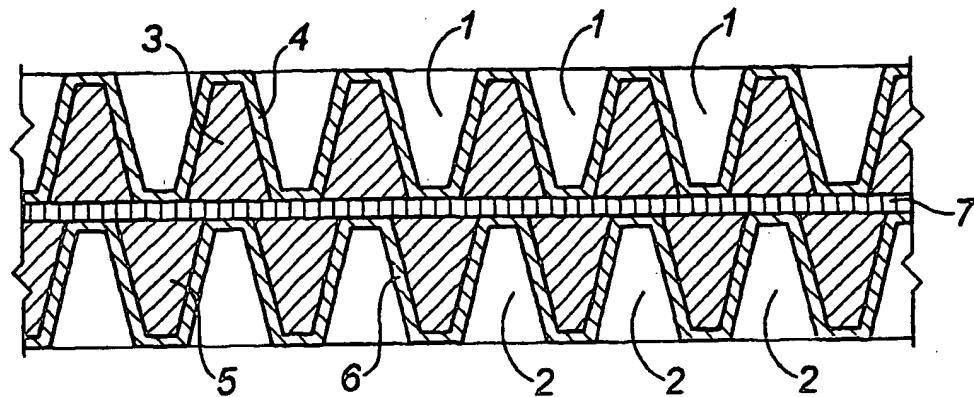
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(54) Title: METAL-SUPPORTED SOLID ELECTROLYTE ELECTROCHEMICAL CELL AND MULTI CELL REACTORS INCORPORATING SAME



(57) Abstract: The invention provides a metal-supported solid electrolyte electrochemical cell, multi cell reactor assemblies incorporating a plurality of such cells, and processes of forming the electrochemical cells. In one embodiment, the electrochemical cell includes a central electrolyte membrane, first and second perforated metallic layers adhered to each of the major surfaces of the central electrolyte membrane, and first and second outer, non-porous electrolyte layers formed above the metallic layers. In another embodiment, first and second inner, porous electrolyte layers are sandwiched on either side of the central membrane, between the first and second metallic layers. The electrochemical cell is thus generally formed from ceramic material as thin layers supported on non-porous, robust metallic layers, designed to behave as though made of metal. Preferably, the electrochemical cell includes metallurgically bonded electrical interconnects and/or gas seals.

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 02/00582

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7	H01M8/12	H01M8/24	B01D53/32	B01J19/00	C01B3/38
					C01B13/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 409 371 A (GORDON ARNOLD Z) 25 April 1995 (1995-04-25)  column 6, line 3-11 claims 1,5; figure 3 ---	1,2,9, 11,12, 18,20,22
A	US 5 298 342 A (BENJAMIN THOMAS G ET AL) 29 March 1994 (1994-03-29) claim 1 ---	1-47
A	EP 0 171 910 A (NGK INSULATORS LTD) 19 February 1986 (1986-02-19) the whole document ---	1-47

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 02/00582

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 11, 26 December 1995 (1995-12-26) & JP 07 201347 A (TOSHIBA CORP), 4 August 1995 (1995-08-04) abstract ---	1-47
A	US 3 525 646 A (TANNENBERGER HELMUT ET AL) 25 August 1970 (1970-08-25) claims 1,7-9 ---	1-47
A	WO 89 11739 A (STANFORD RES INST INT) 30 November 1989 (1989-11-30) claims 11,23,24,28 figures 15,22 ----	1-47

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